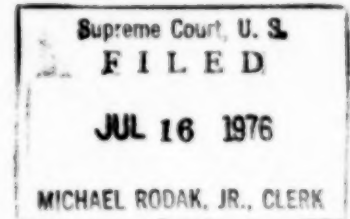


**APPENDIX  
EXHIBIT VOLUME**



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**In the Supreme Court of the United States**

OCTOBER TERM, 1976

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No. 75-978

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E. I. DU PONT DE NEMOURS AND  
COMPANY, *et al.*, Petitioners,

v.

RUSSELL E. TRAIN, *as Administrator,*  
*Environmental Protection Agency,*  
*et al.*, Respondents

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**On Writ Of Certiorari To The United States Court  
Of Appeals For The Fourth Circuit**

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**Petition for Certiorari Filed January 12, 1976  
Certiorari Granted April 19, 1976**

**In the Supreme Court of the United States**

OCTOBER TERM, 1976

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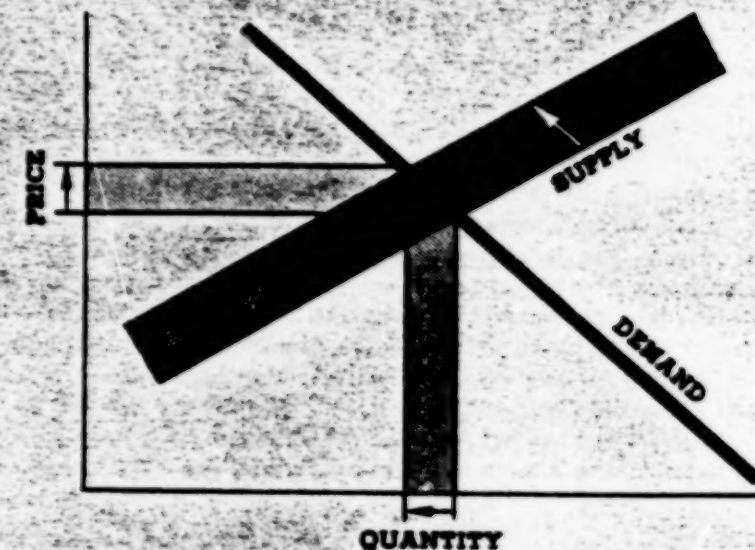
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EPA-230/2-74-015

APRIL 1974

## ECONOMIC ANALYSIS OF EFFLUENT GUIDELINES FOR THE INORGANIC CHEMICALS INDUSTRY

*Phase I*



U.S. ENVIRONMENTAL PROTECTION AGENCY  
Office of Planning and Evaluation  
Washington, D.C. 20460



5419A

ECONOMIC ANALYSIS OF EFFLUENT GUIDELINES  
FOR  
THE INORGANIC CHEMICALS INDUSTRY

April 1974

Contract No. 68-01-1541

Office of Planning and Evaluation  
Environmental Protection Agency  
Washington, D.C. 20460

PREFACE

The attached document is a contractor's study prepared with the supervision and review of the Office of Planning and Evaluation of the U.S. Environmental Protection Agency (EPA). Its purpose is to provide a basis for evaluating the potential economic impact of effluent limitations guidelines and standards of performance established by EPA pursuant to sections 304(b) and 306 of the Federal Water Pollution Control Act.

The study supplements an EPA technical "Development Document" issued in conjunction with the promulgation of guidelines and standards for point sources within this industry category. The Development Document surveys existing and potential waste treatment and control methods and technologies within this category and presents the investment and operating costs associated with various control technologies. This study supplements that analysis by estimating the broader economic effects (including product price increases, continued viability of affected plants, industry growth and foreign trade) of the required application of certain of these control technologies.

This study has been submitted in fulfillment of Contract No. 68-01-1541, Task No. 30 by Arthur D. Little, Inc. Work was completed as of April 1974. The study is based primarily upon an earlier study, also prepared by Arthur D. Little, Inc., entitled "Economic Analysis of Proposed Effluent Guidelines for Inorganic Chemicals, Alkali and Chlorine Industries." The earlier report was circulated in conjunction with the publication in the Federal Register of a notice of proposed rulemaking under sections 304(b) and 306 for the subject point source category. The analysis contained in the original study has been revised based upon information received during the period of time between publication of the notice of proposed rulemaking and the promulgation of the final regulation. Because of the constraints of time, the control and treatment costs analyzed in this study may not in all instances be identical to those associated with the requirements of the promulgated regulation. However, those differences, when they exist, are minor insofar as the final conclusions of the study are concerned.

This report represents the conclusions of the contractors. It has been reviewed by the Office of Planning and Evaluation and approved for publication. Approval does not signify that the contents necessarily reflect the views of the Environmental Protection Agency. The study has been considered, together with the Development Document, information received in the form of public comments on the proposed regulation, and other materials in the establishment of final effluent limitations guidelines and standards of performance.

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## I. SUMMARY

### A. INTRODUCTION

The following report is submitted in compliance with Task Order No. 30 to BOA No. 68-01-1541, "Economic Impact of 1972 Federal Water Pollution Control Amendments on the Inorganic Chemical Industry." As outlined in our proposals, this report deals with 24 inorganic chemicals, including the nine discussed in the initial study;<sup>1</sup>

Aluminum Chloride  
Aluminum Sulfate  
Chlorine and Caustic Soda  
Hydrochloric Acid  
Hydrofluoric Acid  
Hydrogen Peroxide  
Lime  
Nitric Acid  
Sulfuric Acid

as well as the six inorganic chemicals studied in depth;

Calcium Carbide  
Sodium Sulfate  
Titanium Dioxide (Chloride)  
Titanium Dioxide (Sulfate)  
Sodium Chromate and Bichromate  
Potassium Bichromate

and the nine additional products briefly reviewed in a subsequent analysis;

Sodium Bicarbonate  
Solar Salt  
Evaporated Salt  
Sodium Silicate  
Sodium Metal  
Sodium Sulfite  
Calcium Chloride  
Synthetic Soda Ash and  
Potassium Sulfate.

<sup>1</sup>"Initial Analysis of the Economic Impact of Water Pollution Control Costs Upon Ten Inorganic Chemicals," report to Environmental Protection Agency by Booz, Allen Public Administration Services, Inc., January 5, 1973.

The objective of this study was to analyze the economic impact of the costs of water pollution abatement requirements for the specified products, using the data for the nine initial study products contained in the initial impact study, new water treatment cost data provided by EPA and the industry information developed for the major study products and the additional study products by the contractor.

## B. IMPACT ANALYSIS METHODOLOGY

In order to assess the impact of water treatment costs on the inorganic chemicals covered in this report, we have developed an analytical framework to arrive at the impact judgment. In addition to providing us with a systematic method to weigh each of the factors affecting the impact judgment, the methodology also provides a format by which the basis for our conclusions are clearly presented.

The basic premise behind the methodology is that a producer faced with new investment in water treatment facilities could (1) continue to operate by (a) passing on the additional costs through price increases, or (b) absorbing the costs (thereby reducing profits); or (2) shut his plant down. This premise, of course, reduces the impact of increased costs due to water treatment to the simplest terms. In the real world, the result of higher costs most probably would be some combination of these alternatives, e.g., a price hike by the most efficient producer sufficient to recover part of his costs (but not enough to cover most of the costs of the marginal producer), reduced profit margins for the most efficient producer partially offset by an increased market share resulting from plant shutdowns by the marginal producer(s).

The approach we have taken in assessing the impact on each of the inorganic chemicals is to first examine the likelihood that the higher costs imposed on the industry by virtue of new water effluent guidelines will be defrayed, wholly or in part, by higher product prices. If the conclusion is that treatment costs cannot be passed on through price increases, the second part of the impact analysis is to examine the likelihood that some plants in the industry would be forced to shut down, taking into account both economic and noneconomic factors.

### 1. Price Increase Constraints

The treatment costs per ton before taxes indicate the magnitude of the unit price increase necessary to fully recover all treatment costs (i.e., repay the investment and cover operating costs). The larger the ratio of before-tax unit treatment cost to actual unit selling price, the more difficult it will be to fully recover treatment costs, all things being equal. As indicated, the first question we have addressed is whether conditions in the specific competitive situation would permit price increases. In general, the products' price history and the nature of those prices--whether firm or widely dispersed and discounted--provide a clue

as to the possibility of price increases. More specifically, however, the following factors are those that we have used in arriving at the judgment as to whether price increases are feasible. Except in unusual circumstances, no one factor would be overriding. Rather, the judgment is based on a combination of factors.

Substitute Products (or Processes)--If substitute products exist, price increases to cover the (full) costs of water treatment would be difficult.

Capacity Utilization--If capacity utilization for the industry is low, price increases to cover the (full) costs of treatment would be difficult.

Captive Usage--If there is negligible captive use, price increases to cover the (full) costs of water treatment would be difficult.

Demand Growth--Price increases are more difficult to achieve in a static or declining market than in a growing market.

Foreign Competition--If the market can be served by foreign competitors (particularly if the foreign producers are not faced with added water pollution abatement costs), price increases are less likely.

Abatement Cost Differences--If some plants in the industry will incur substantially higher water pollution abatement expenditures than other plants, they will be less able to pass on the added costs as price increases.

Price Elasticity of Demand--For some products, substantial water pollution abatement costs, if passed on as price increases, could result in reduced demand for the product.

Basis for Competition--If the basis for competition in the industry is primarily price as opposed to service or technology, cost increases will be more difficult to pass on, particularly if there is a significant difference between unit treatment costs between large producers and small producers.

Market Share Distribution--If the market share distribution is fragmented (rather than concentrated, in which case there often is a dominant price leader), price increases are less likely, particularly if treatment costs do not affect all producers fairly equally.

Number of Producers--If the market is served by many producers (increasing the likelihood of manufacturing cost differences, abatement cost differences, etc.), a condition exists constraining price increases.

Although not explicitly listed in the generic model, we have been alert to other factors which might prevail for individual products. For example, the economic importance of a product in the manufacturing costs of derivative products might act as a constraint on price increases.



In assessing the possibility of water treatment costs being passed on as titanium dioxide price increases, for instance, we took into account the impact on titanium dioxide demand of the resultant increase in the cost of paint.

## 2. Plant Shutdown Factors

If treatment costs cannot be passed on as price increases, the simplistic model says that the producer either absorbs them or shuts down his plant. The shutdown decision will involve both economic and strategic (i.e., noneconomic) considerations as follows.

Profitability--The after-tax cost per ton of water treatment compared with unit after-tax net income measures the producer's ability or willingness to absorb the added cost.

Cash Flow--Plants will continue to operate temporarily at essentially zero profitability (if necessary) if the plant is producing a positive cash flow (and has a competitive process and is in a stable or growing market).

Ratio of Investment in Treatment Facilities to Net Fixed Investment--If the new investment in water treatment facilities bulks large in comparison with existing plant investment (and other factors are marginal), a shutdown decision may be in order. In some instances, the availability (and cost) of capital to the producer may influence the shutdown decision.

Integration--The degree of backward or forward integration is a factor in the shutdown decision. A producer (or industry) with a significant raw material position or one using the product for downstream manufacture is less likely to curtail production than a non-integrated producer (or industry).

Chemical Complex--An isolated plant would be unable to take advantage of common treatment facilities.

Other Environmental Problems--If a plant has already committed funds for air pollution, it will be more likely to commit the additional funds necessary for water pollution. Alternately, if a company faces both water and air pollution abatement (and/or unusual OSHA) costs, the magnitude of the environmental costs taken together may prompt plant closing whereas any one taken alone would not.

Emotional Commitment--The emotional commitment of the company to that particular product (taking into account protection of competitive position, prestige, the importance of the product in the company's long-range strategy, etc.) may be a factor in the shutdown decision.

Ownership--Other things being equal (and negative), multi-industry companies are more likely to shut down marginal plants than less-diversified producers. The premise is that the multi-industry producer has other (and better) investment opportunities than the single product company (particularly a privately-held, family business).

## C. INITIAL AND MAJOR STUDY PRODUCTS

### 1. Water Treatment Costs

All of the water treatment costs for the various levels of effluent control shown in this report were taken from the Development Document for Proposed Effluent Limitations Guidelines and New Source Performance Standards for the Major Inorganic Products prepared for the EPA under contract number 68-01-1513 dated June 1973. The water treatment costs (on a before-tax basis) by product are summarized in Table 1. Base-level practice (B.L.P.) represents water treatment practices which, in the judgment of the Development Document, are followed by most of the industry and exceeded by exemplary plants. Similarly, exemplary plant practice (E.P.P.) reflects the unit cost of water treatment and control practices at the exemplary plant. Proposed best practicable technology (B.P.T.) reflects the Development Document's estimate of the unit water treatment cost for the product in question based upon the best technically and economically feasible treatment and control technology. Finally, proposed best available technology (B.A.T.) reflects the degree of effluent reduction which must be achieved by July 1, 1983. The unit treatment costs used for any particular level of control in the impact analysis is the incremental cost over B.L.P.

### 2. Manufacturing Costs and Profitability

In the following report the manufacturing costs and profitability data shown in Table 2 for the "Initial Study Products" were taken from the initial study project. Comparable data for the six "Major Study Products" were developed by the Contractor.

### 3. Conclusions

In Figure 1 we have compared the incremental (over B.L.P.) water treatment costs estimated in the Development Document to achieve B.A.T. effluent standards as a function of product selling price versus treatment costs as a function of unit profit margin for the inorganic chemicals discussed in this study. Three initial study products do not appear on the figure because data for industry profitability were not developed. For the three products (hydrochloric acid, nitric acid, and hydrogen peroxide), however, unit treatment costs are small so that these products would appear in the lower left-hand corner of the figure. One of the major study products, viz. calcium carbide, has also been left off the figure. With a treatment cost of \$1.94 per ton versus a selling price of \$90 per ton, the cost/price ratio is a nominal 2.2%. However, since industry profit margins are minimal, the treatment cost as a function of unit margins is very high and falls off the scale of the figure.

Titanium dioxide stand out in this figure as the product where the estimated treatment costs represent the highest proportion of both selling price and profit margin. (For both the chloride and sulfate

TABLE 1

**WATER TREATMENT COSTS BY LEVELS OF CONTROL**  
(Dollars Per Ton of Product)

	Base- Level Practice	Exemplary Plant Practice	Best Practicable Technology	Best Available Technology
<b>Initial Study Products</b>				
Aluminum Chloride	0.00	3.77	3.77	3.77
Aluminum Sulfate	0.79	1.72	1.72	1.72
Chlorine				
(Mercury)	2.14	2.14	2.74	3.00
(Diaphragm)	0.04	0.29	0.29	0.56
Hydrochloric Acid	0.25	0.25	0.30	0.30
Hydrofluoric Acid	3.57	4.04	4.89	12.95
Hydrogen Peroxide				
(Organic)	0.20	0.33	1.06	1.06
(Electrolytic)	0.00	0.75	1.14	1.14
Lime				
(Bag)	0.00	0.00	0.00	0.00
(H <sub>2</sub> O Scrubber)	0.00	1.28	1.28	1.28
Nitric Acid	0.00	0.22	0.22	0.22
Sulfuric Acid				
(Burning)	0.05	0.10	0.17	0.17
(Regen)	0.25	0.75	0.75	0.75
<b>Major Study Products</b>				
Calcium Carbide	0.00	1.94	1.94	1.94
Sodium Sulfate	0.00	0.00	0.00	0.00
Titanium Dioxide				
(Sulfate)				
[Neutralization]	1.90	10.05	83.57	98.09
[Acid Recovery]	1.69	10.05	35.71	50.48
(Chloride)	2.12	38.61	38.61	66.79
Sodium Chromate and	0.26	11.66	16.45	16.45
Bichromate				
Potassium Bichromate	0.57	3.52	5.24	5.24
<b>Additional Products</b>				
Sodium Bicarbonate	0.03	0.04	0.04	0.04
Solar Salt	2.34	2.34	2.34	2.34
Evaporated Salt	0.00	0.23	0.44	0.44
Sodium Silicate	0.19	0.60	1.14	1.14
Sodium Metal	0.19	3.07	5.53	5.53
Sodium Sulfite	0.00	3.09	2.98	(1.56)*
Calcium Chloride	0.00	0.19	0.19	0.19
Soda Ash--Synthetic	0.44	(1.17)*	0.44	1.10
Potassium Sulfate	0.10	2.47	2.47	2.47

\*Before-tax profit.

Source: Development Document on inorganic chemicals, alkali and chlorine industries prepared for United States Environmental Protection Agency under Contract Number 68-01-1513, June 1973.

TABLE 2

**MANUFACTURING COSTS AND PLANT ECONOMICS**

	Selling Price	Manufacturing Cost <sup>1</sup> (\$/Ton)	After Tax Net Income	Depreciable Investment \$MM	Sample Plant Capacity M Tons/Year
<b>Initial Study Products</b>					
Aluminum Chloride	292	226	21	1.2	10
Aluminum Sulfate	42	32	3	1.0	33
Chlorine and Caustic Soda					
Mercury	101 <sup>2</sup>	N.A.	4.12	13	66
Diaphragm	101 <sup>2</sup>	81	4.33	20	115
Hydrofluoric Acid	370	N.A.	18	5	21
Lime	16	12	1.00	4	165
H <sub>2</sub> SO <sub>4</sub> Burning	20	14	1.20	6	330
Regeneration	22	16	1.20	9	330
<b>Major Study Products</b>					
Calcium Carbide	90	86	0	4	45
Titanium Dioxide--					
Sulfate	540	416	26	15	25
Chloride	570	471	21	21	25
Sodium Bichromate	245	212	18	5	49
Potassium Bichromate	475	403	24	2	5

<sup>1</sup>Excluding GS&A and federal income taxes.

<sup>2</sup>Sales revenue per ECU.

Source: Initial Study Products: "Initial Analysis of the Economic Impact of Water Pollution Control Costs Upon Ten Inorganic Chemicals," final report to Environmental Protection Agency for Booz, Allen Public Administration Services, Inc., January 5, 1973.  
Major Study Products: The Contractor.



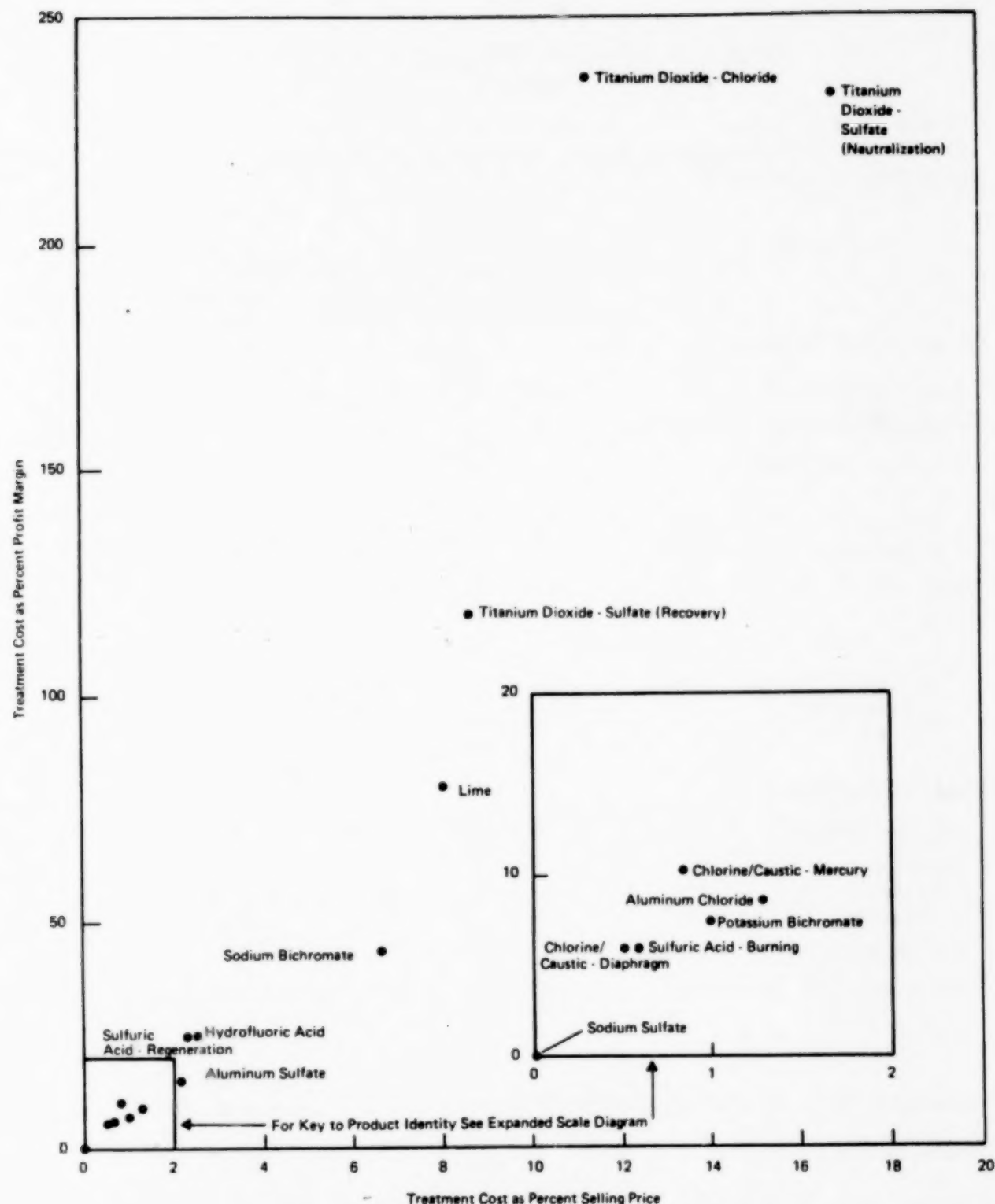


FIGURE 1 INCREMENTAL WATER TREATMENT COSTS FOR BEST AVAILABLE TECHNOLOGY VERSUS SELLING PRICE AND PROFIT MARGIN

process, the estimated treatment costs on a unit basis are very nearly 2.5 times current estimated industry profit levels.) Lime and sodium bichromate are at an intermediate level where treatment costs represent 7-8% of selling price and 50-80% of estimated profit margins. A third group of products--hydrofluoric acid, sludge sulfuric acid, and aluminum sulfate--are faced with treatment costs representing 2-3% of selling price and 15-25% of estimated profit margins. A final group of products including aluminum chloride, potassium bichromate, chlorine and caustic soda, and direct burning sulfuric acid, have estimated treatment costs at about 1% of selling price and 5-10% of profits. No water treatment costs were ascribed to sodium sulfate (as chromate by-product).

The same comparison is made in Figure 2 using incremental water treatment costs for B.P.T. In general, the spatial relationships between the identified products is much the same as in Figure 1, with the exception that sulfate process titanium dioxide is at a greater disadvantage with respect to chloride process titanium dioxide.

Although Figures 1 and 2 provide a first approximation of the impact severity on each of the products from additional water treatment costs, we have used the methodology described above to assess the economic impact. The results of this assessment are summarized in Table 3. From this table and based on the treatment costs given in the Development Document we conclude that plant shutdowns as a direct result of increased water treatment costs using B.A.T. are likely for chlorine/caustic soda, lime, sludge sulfuric acid, sulfate process titanium dioxide and sodium bichromate. Although the B.A.T. costs for potassium bichromate could be passed on through a price increase the one significant manufacturing facility could not continue operating if the sodium bichromate plant upon which it depends were shut down. For the other products included in the study the increased water treatment costs will either be passed on as price increases or absorbed by the producers.

The final effluent guidelines, published in the March 12, 1974, Federal Register contain some changes from the originally proposed guidelines. Among others, the B.A.T. standards for mercury cell chlorine/caustic and sulfate process titanium dioxide have been modified to allow higher suspended solids. The aforementioned plant shutdown conclusions are based on the guidelines and estimated treatment costs contained in the original Development Document dated June 1973.

The same shutdown conclusions pertain as well for B.P.T. For three of the five shutdown candidates--viz. lime, sludge sulfuric acid, and sodium bichromate--B.P.T. costs are identical to B.A.T. costs. It should be noted that the regulation as promulgated for B.P.T. standards for sodium bichromate has been relaxed somewhat from the originally proposed regulation. For the remaining two--viz. mercury cell chlorine/caustic and sulfate process titanium dioxide--the costs resulting from B.P.T. were not judged to be significantly different (i.e., lower) than B.A.T. costs to impact the industries less severely.

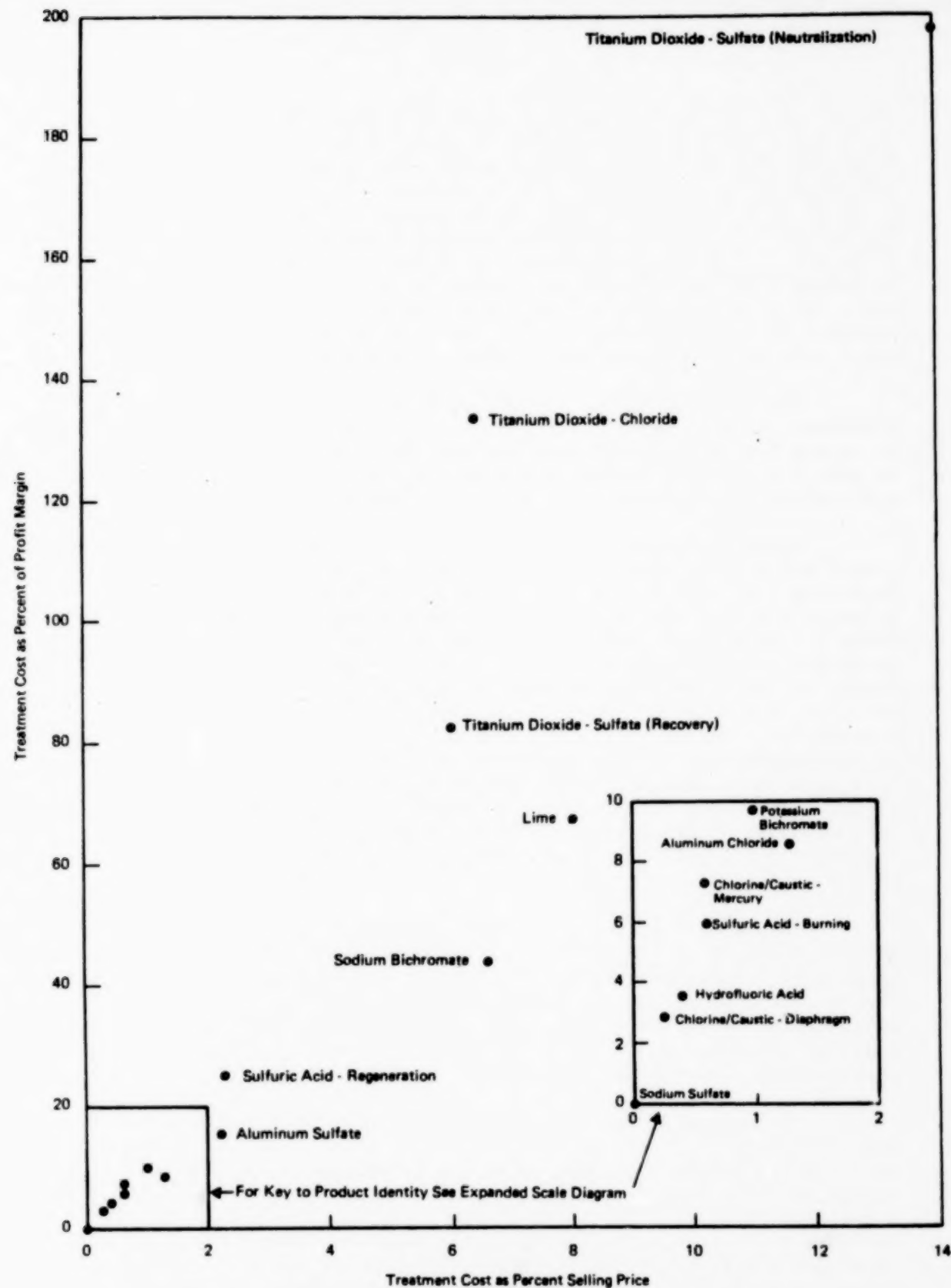


FIGURE 2 INCREMENTAL WATER TREATMENT COSTS FOR BEST PRACTICABLE TECHNOLOGY VERSUS SELLING PRICE AND PROFIT MARGIN

## D. ADDITIONAL STUDY PRODUCTS

### 1. Water Treatment Costs

All of the water treatment costs for the various levels of effluent control shown in this report were taken from the Development Document prepared for the EPA under contract number 68-01-1513 dated June 1973.

The water treatment costs provided by the Development Document and summarized in Table 1 were specific to a particular manufacturing process for each of the products under consideration. In general, this manufacturing process is not the only method for producing the products being considered, or in some cases not even the major method of production. Our judgment of economic impact, however, is necessarily predicated on these costs and we have, therefore, confined our judgment to the economic impact on the producers utilizing the particular process defined by the Development Document. The processes are specified in the individual product studies.

### 2. Conclusions

The impact analysis matrix (Table 3) also summarizes the relevant price increase and plant shutdown impact considerations for the additional products. For none of the nine additional products do we see plant shutdowns as a direct result of increased water treatment costs. For one of the nine--sodium metal--there may be plant shutdowns as a result of possible reduced demand for alkyl leads in gasoline.

The Development Document indicates that for solar salt there would be no incremental cost for B.P.T. or B.A.T. over E.P.P. and consequently no economic impact. For sodium bicarbonate, evaporated salt, sodium silicate, and calcium chloride, the conclusion is that water treatment costs can be passed on as price increases. For sodium metal, sodium sulfite, and potassium sulfate, the water treatment costs will either be absorbed by the producer or passed on as price increases. Finally, for sodium carbonate the nominal incremental cost for B.A.T. over E.P.P. will be absorbed by the producer. (The original Development Document indicates that there is no incremental cost over E.P.P. for B.P.T. for synthetic soda ash.)

TABLE 3  
IMPACT ANALYSIS MATRIX

1972 Production (M Tons) 1971 Unit Value (\$/Ton) 1972 Production Value (\$MM) Number of Plants (Current)	PRICE INCREASE CONSTRAINTS			ALUMINUM CHLORIDE	ALUMINUM SULFATE	CHLORINE & CAUSTIC SODA (Mercury)	CHLORINE & CAUSTIC SODA (Diaphragm)
	Factor	Condition for Constraint	Treatment Level				
	Ratio of Bt* Treatment Cost to Selling Price (%)	High	E.P.P. B.P.T. B.A.T.	34 292 9.4 8	1,124 42.50 47.8 100	9,870 (Cl <sub>2</sub> ); 45.50 (Cl <sub>2</sub> ); 464 (Cl <sub>2</sub> ); 29**	10,710 (NaOH) 47.80 (NaOH) 525 (NaOH) 34**
	Substitute Products	High Occurrence		Low	Low	0.0 0.6 0.8	0.25 0.25 0.52
	Capacity Utilization	Low		65%	ca. 75%		95%
	Captive Usage	Low		Low	<10%	62% (Cl <sub>2</sub> );	33% (NaOH)
	Demand Growth	Low		Static	3%/Yr	6%/Yr (Cl <sub>2</sub> );	5% (NaOH)
	Foreign Competition	High		Low	< 1%		Low
	Abatement Cost Differences	Unequal		Equal	Unequal		Unequal
	Price Elasticity of Demand	High		Low	Low		Low to Moderate
	Basis for Competition	Price		Quality, Service	Price		Price
	Market Share Distribution	Fragmented		Fragmented	Concentrated		Concentrated
	Number of Producers	Many		6	27		30

\*Before-Tax.

\*\*Includes five combined (both mercury and diaphragm) plants.

TABLE 3 (Continued)

PLANT SHUTDOWN DECISION	Factor	Condition for Shutdown	Treatment Level	ALUMINUM CHLORIDE	ALUMINUM SULFATE	CHLORINE & CAUSTIC SODA (Mercury)	CHLORINE & CAUSTIC SODA (Diaphragm)
	Ratio of At* Treatment Cost to At* Net Income (%)	High	E.P.P. B.P.T. B.A.T.	8.6 8.6 8.6	15.7 15.7 15.7	0.0 7.3 10.4	2.9 2.9 6.0
	Cash Flow (Including Treatment Costs)	Negative		N.A.	Positive	Positive	Positive
	Ratio of Investment in Treatment Facilities to Net Fixed Investment (%)	High	E.P.P. B.P.T. B.A.T.	N.A. N.A. N.A.	10.0 10.0 10.0	0.0 1.5 1.9	0.03 0.72 2.4
	Integration	Low		Moderate Forward; Low Backward	Low	High	
	Chemical Complex	Isolated Plant		Isolated	Complex and Isolated	Complex	
	Other Environmental Problems (Including OSHA)	Multiple		Air Pollution	Solid Waste	Nominal	
	Emotional Commitment	Indifference		High	Low to Moderate	Low to High	
	Ownership	Multi-Industry Companies		Predominantly Multi-Industry	Multi-Industry	Multi-Industry	

\*After-Tax.



TABLE 3 (Continued)

PRICE INCREASE CONSTRAINTS				HYDROCHLORIC ACID	HYDROFLUORIC ACID	HYDROGEN PEROXIDE (Electrolytic)	HYDROGEN PEROXIDE (Organic)
Factor	Condition for Constraint	Treatment Level					
1972 Production (M Tons) 1971 Unit Value (\$/Ton) 1972 Production Value (\$M) Number of Plants (Current)				2,204 43.2 95.2 89	332.2 349.31 112.8 14	9 596 5.4 1	66 596 39.3 5
Ratio of MT Treatment Cost to Selling Price (%)	High	E.P.P. B.P.T. B.A.T.		0.0 0.2 0.2	0.1 0.4 2.5	0.1 0.2 0.2	0.1 0.1 0.2
Substitute Products	High Occurrence			Moderate	Low	Low	Low
Capacity Utilization	Low			ca. 90%	84.5%		70%
Captive Usage	Low			60%	75%		30%
Demand Growth	Low			4%/Yr	5%-7%/Yr		Static
Foreign Competition	High			Low	Low		Moderate
Abatement Cost Differences	Unequal			Unequal	Equal		Unequal
Price Elasticity of Demand	High			Moderate	Low		Low
Basis for Competition	Price			Price	Price		Quality, Service
Market Share Distribution	Fragmented			Fragmented	Concentrated		Concentrated
Number of Producers	Many			42	9		6

TABLE 3 (Continued)

PLANT SHUTDOWN DECISION				HYDROCHLORIC ACID	HYDROFLUORIC ACID	HYDROGEN PEROXIDE (Electrolytic)	HYDROGEN PEROXIDE (Organic)
Factor	Condition for Shutdown	Treatment Level					
Ratio of AT Treatment Cost to AT Net Income (%)	High	E.P.P. B.P.T. B.A.T.		N.A. N.A. N.A.	1.3 3.6 25.4	N.A. N.A. N.A.	N.A. N.A. N.A.
Cash Flow (Including Treatment Costs)	Negative			Positive	Positive		N.A.
Ratio of Investment in Treatment Facilities to Net Fixed Investment (%)	High	E.P.P. B.P.T. B.A.T.		N.A. N.A. N.A.	0.6 1.0 1.5	N.A. N.A. N.A.	N.A. N.A. N.A.
Integration	Low			High	High Forward	Moderate Forward; Moderate Backward	
Chemical Complex	Isolated Plant			Complex	Complex		Isolated
Other Environmental Problems (Including OSHA)	Multiple			Air	Nominal		None
Emotional Commitment	Indifference			High	High		High
Ownership	Multi-Industry Companies			Multi-Industry	Multi-Industry		Multi-Industry

TABLE 3 (Continued)

Factor	PRICE INCREASE CONSTRAINTS		LIME	NITRIC ACID	SULFURIC ACID (Burning)	SULFURIC ACID (Regen)
	Condition for Constraint	Treatment Level				
1972 Production (M Tons)			20,865	7,000		31,086
1971 Unit Value (\$/Ton)			16	67		21
1972 Production Value (\$MM)			334	441		652.8
Number of Plants (Current)			170	80	142 Total;	33 Regen
Ratio of BT Treatment Cost to Selling Price (%)	High	E.P.P. B.P.T. B.A.T.	8.0 8.0 8.0	N.A. N.A. 0.3	0.2 0.6 0.6	2.3 2.3 2.3
Substitute Products	High Occurrence		Low	Moderate		Moderate
Capacity Utilization	Low		ca. 95%	85%	65-70% (Fertilizer) 95% (Merchant)	
Captive Usage	Low		35%	90%	60%	
Demand Growth	Low		Moderate	Low	3-4% (Fertilizer) 2-3% (Merchant)	
Foreign Competition	High		Low	Low	Low	
Abatement Cost Differences	Unequal		Unequal	Equal	Unequal	
Price Elasticity of Demand	High		Moderately High	Moderate	Moderate	
Basis for Competition	Price		Price	Price	Price	
Market Share Distribution	Fragmented		Fragmented	Fragmented	Concentrated (Fertilizer) Fragmented (Merchant)	
Number of Producers	Many		110	49	71	

TABLE 3 (Continued)

Factor	PLANT SHUTDOWN DECISION		LIME	NITRIC ACID	SULFURIC ACID (Burning)	SULFURIC ACID (Regen)
	Condition for Shutdown	Treatment Level				
Ratio of AT Treatment Cost to AT Net Income (%)	High	E.P.P. B.P.T. B.A.T.	67.0 67.0 67.0	N.A. N.A. N.A.	2.5 6.0 6.0	25 25 25
Cash Flow (Including Treatment Costs)	Negative		ca. \$2/Ton Depr.	N.A.	Positive	Positive
Ratio of Investment in Treatment Facilities to Net Fixed Investment (%)	High	E.P.P. B.P.T. B.A.T.	N.A. N.A. N.A.	N.A. N.A. N.A.	1.4 3.0 3.0	14.4 14.4 14.4
Integration	Low		Moderate Forward; High Backward	High Forward; Low Backward	Moderate to High	
Chemical Complex	Isolated Plant		Complex and Isolated	Complex	Complex	
Other Environmental Problems (Including OSHA)	Multiple		Air	Air Pollution	Air Pollution	
Emotional Commitment	Indifference		High	Moderate	High	
Ownership	Multi-Industry Companies		Two-thirds are Multi-Industry	Large Multi-Industry; Small Fertilizer and Explosive	Multi-Industry	

TABLE 3 (Continued)

PRICE INCREASE CONSTRAINTS				TITANIUM DIOXIDE (Sulfate)	TITANIUM DIOXIDE (Chloride)
Factor	Condition for Constraint	Treatment Level	CALCIUM CARBIDE		
1972 Production (M Tons) 1971 Unit Value (\$/Ton) 1972 Production Value (\$MM) Number of Plants (Current)			493 90 44.4 5	1,364 21 28.6 32	687 452 343 8
Ratio of BT Treatment Cost to Selling Price (X)	High	E.P.P. B.P.T. B.A.T.	2.2 2.2 2.2	0.0 0.0 0.0	1.5 6.0 8.6 6.4 6.4 11.3
Substitute Products	High Occurrence		High	High	Low
Capacity Utilization	Low		59%	88%	
Captive Usage	Low		75	Low	
Demand Growth	Low		Declining	Static	
Foreign Competition	High		Low	Moderate to High	Low
Abatement Cost Differences	Unequal		Unequal	Unequal	Unequal
Price Elasticity of Demand	High		Moderately High	High	Low
Basis for Competition	Price		Price	Price	Technology and Service
Market Share Distribution	Fragmented		Concentrated	Fragmented	Concentrated
Number of Producers	Many		4	22	4 7

TABLE 3 (Continued)

PLANT SHUTDOWN DECISION			CALCIUM CARBIDE	SODIUM SULFATE	TITANIUM DIOXIDE (Sulfate)	TITANIUM DIOXIDE (Chloride)
Factor	Condition for Shutdown	Treatment Level				
Ratio of AT Treatment Cost to AT Net Income (X)	High	E.P.P. B.P.T. B.A.T.	0.0 0.0 0.0	0.0	Neut. 19.7 198.0 233.0 Acid Rec. 20.3 82.5 118.0	134 134 237
Cash Flow (Including Treatment Costs)	Negative		N.A.	N.A.	Positive	
Ratio of Investment in Treatment Facilities to Net Fixed Investment (X)	High	E.P.P. B.P.T. B.A.T.	N.A. N.A. N.A.	0.0 0.0 0.0	0.2 48.3 55.6 0.2 19.0 26.3	17.3 17.3 23.5
Integration	Low		Moderate Forward; High Backward	High	Low to Moderate Forward; Moderate Backward	Low to Moderate Forward; Low to Moderate Backward
Chemical Complex	Isolated Plant		Complex and Isolated	Complex	Isolated	
Other Environmental Problems (Including OSMA)	Multiple		Air Pollution	Some Air Pollution	Solid Waste Air (Chloride)	
Emotional Commitment	Indifference		Acetylene Low; Others High	By-product Low; Others High	High	
Ownership	Multi-Industry Companies		Primarily Multi-Industry	Multi-Industry	Multi-Industry	



TABLE 3 (Continued)

PRICE INCREASE CONSTRAINTS			SODIUM CHROMATE AND BICHRONATE	POTASSIUM BICHRONATE	SODIUM BICARBONATE	SOLAR SALT
Factor	Condition for Constraint	Treatment Level				
1972 Production (M Tons) 1971 Unit Value (\$/Ton) 1972 Production Value (\$MM) Number of Plants (Current)			137.1 248 24.9 3	3 475 1.4 1	248 49 12.1 4	1,799* 8.40** 15.1*** 18
Ratio of BT Treatment Cost to Selling Price (%)	High	E.P.P. B.P.T. B.A.T.	4.6 6.6 6.6	0.6 1.0 1.0	0.02 0.02 0.02	0.00 0.00 0.00
Substitute Products	High Occurrence		Many (for derivatives)	Moderate	Low	High
Capacity Utilization	Low		80%	N.A.	94%	High
Captive Usage	Low		35%	Low	Low	Low
Demand Growth	Low		Declining	Low	4½-6%	Static
Foreign Competition	High		High	Moderate	Low	High
Abatement Cost Differences	Unequal		Unequal	---	Equal	None
Price Elasticity of Demand	High		High	High	Low	High
Basis for Competition	Price		Price and Service	Price	Price	Price
Market Share Distribution	Fragmented		Concentrated	Concentrated	Concentrated	Fragmented
Number of Producers	Many		3	1	3	11

\*Quantity sold or used by producers.

\*\*Reported 1972 value.

\*\*\*Value of quantity sold or used by producers.

TABLE 3 (Continued)

PLANT SHUTDOWN DECISION			SODIUM CHROMATE AND BICHRONATE	POTASSIUM BICHRONATE	SODIUM BICARBONATE	SOLAR SALT
Factor	Condition for Shutdown	Treatment Level				
Ratio of AT Treatment Cost to AT Net Income (%)	High	E.P.P. B.P.T. B.A.T.	30.8 43.7 43.7	6.2 9.7 9.7	0.2 0.2 0.2	0.0 0.0 0.0
Cash Flow (Including Treatment Costs)	Negative		Positive	Positive	Positive	Unchanged
Ratio of Investment in Treatment Facilities to Net Fixed Investment (%)	High	E.P.P. B.P.T. B.A.T.	15.8 29.8 29.8	0.5 1.0 1.0	Low Low Low	0.0 0.0 0.0
Integration	Low		Low to Moderate	High Backward; Low Forward	Low	Low
Chemical Complex	Isolated Plant		Isolated	Isolated	Complex	Isolated
Other Environmental Problems (Including OSHA)	Multiple		Multiple	Multiple	Nominal	Multiple
Emotional Commitment	Indifference		High	High	Low to High	Indifference
Ownership	Multi-Industry Companies		Multi-Industry	Multi-Industry	Predominately Multi-Industry	Single-Industry

TABLE 3 (Continued)

PRICE INCREASE CONSTRAINTS			EVAPORATED SALT	SODIUM SILICATE	SODIUM METAL	SODIUM SULFITE
Factor	Condition for Constraint	Treatment Level				
1972 Production (M Tons) 1971 Unit Value (\$/Ton) 1972 Production Value (\$MM) Number of Plants (Current)			4,051* 26.94** 109.1 23	663 86 57 42	159.9 220 33.28 5	460 48 Avg./\$200 Photo 22 7***
Ratio of BT Treatment Cost to Selling Price (%)	High	E.P.P. B.P.T. B.A.T.	0.87 1.6 1.6	0.5 1.0 1.0	1.0 2.0 2.0	6 Avg./1.5 Photo Grade 6 Avg./1.5 Photo Grade -3 Avg./-.8 Photo Grade****
Substitute Products	High Occurrence		Low	Low	Medium	High General; Low Photo Grade
Capacity Utilization	Low		Low	70% (Low)	85% (High)	90%
Captive Usage	Low		Low	25% (Low)	85% (High)	Low
Demand Growth	Low		2.5% Per Year	Low	Low	Low
Foreign Competition	High		Low	Negligible	Low	Low
Abatement Cost Differences	Unequal		Equal	Equal	Unequal	N.A.
Price Elasticity of Demand	High		Low	Low	Low	Low
Basis for Competition	Price		Price/Service	Price	Price	Price
Market Share Distribution	Fragmented		Fragmented	Fragmented (6 producers control 90%)	Concentrated	Fragmented
Number of Producers	Many		12	10	3	5

\*Quantity sold or used by producers.

\*\*Reported 1972 value.

\*\*\*Plants producing merchant material as by-product and primary product (3 plants primary product--photo grade)--excludes plants producing for captive consumption in MSSC pulp.  
\*\*\*\*Applicable only to product which is manufactured for merchant market by direct reaction of SO<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> with subsequent crystallization to obtain dry material.

TABLE 3 (Continued)

PLANT SHUTDOWN DECISION			EVAPORATED SALT	SODIUM SILICATE	SODIUM METAL	SODIUM SULFITE
Factor	Condition for Shutdown	Treatment Level				
Ratio of AT Treatment Cost to AT Net Income (%)	High	E.P.P. B.P.T. B.A.T.	7.3 13.7 13.7	10 20 20	10 25 25	Low Lower Lowest (Negative)
Cash Flow (Including Treatment Costs)	Negative		Positive	Positive	Negative	Negative
Ratio of Investment in Treatment Facilities to Net Fixed Investment (7)	High	E.P.P. B.P.T. B.A.T.	16.9 33.8 33.8	1 2 2	5 5 5	N.A. N.A. N.A.
Integration	Low		Low	Low	High	80% By-product*
Chemical Complex	Isolated Plant		Isolated	Isolated	Isolated	80% By-product*
Other Environmental Problems (Including OSMA)	Multiple		Nominal	N.A.	N.A.	Multiple
Emotional Commitment	Indifference		High	Low	Low-High	Indifference
Ownership	Multi-Industry Companies		Single-Industry	Multi-Industry	Multi-Industry	Multi-Industry

\*Estimated 80% of merchant sales are of sodium sulfite obtained as by-product of phenol or resorcinol production.



TABLE 3 (Continued)

1972 Production (M Tons) 1971 Unit Value (\$/Ton) 1972 Production Value (\$M) Number of Plants (Current)	PRICE INCREASE CONSTRAINTS			CALCIUM CHLORIDE	SYNTHETIC SODA ASH	POTASSIUM SULFATE
	Factor	Condition for Constraint	Treatment Level			
			E.P.P. B.P.T. B.A.T.			
	Ratio of AT Treatment Cost to Selling Price (2)	High	0.5 0.5 0.5	820 39 32 11	4,301 34.60* 148.8 6	402 42.27 16 6 + Minors
	Substitute Products	High Occurrence		Low	High	Moderate
	Capacity Utilization	Low		90%	95%	76% (Nominal 1972)
	Captive Usage	Low		Low	25%	Low
	Demand Growth	Low		Low	Declining	Low
	Foreign Competition	High		Low	Low	Moderate
	Abatement Cost Differences	Unequal		N.A.	Unequal**	Unequal***
	Price Elasticity of Demand	High		Low	High	Low
	Basis for Competition	Price		Price	Price	Price
	Market Share Distribution	Fragmented		Concentrated	Concentrated	Concentrated
	Number of Producers	Many		10	5	5 Plus Minors

\*Reported 1972 value.  
\*\*Unequal in comparison with effluent treatment costs for natural soda ash.  
\*\*\*Between production processes--i.e., Hargreaves, Mannheim, Langbeinite, etc.

TABLE 3 (Continued)

PLANT SHUTDOWN DECISION			CALCIUM CHLORIDE	SYNTHETIC SODA ASH	POTASSIUM SULFATE
Factor	Condition for Shutdown	Treatment Level			
Ratio of AT Treatment Cost to AT Net Income (2)	High	E.P.P. B.P.T. B.A.T.	Low Low Low	77% Profit 0 43.8	16 16 16
Cash Flow (Including Treatment Costs)	Negative		Positive	Positive	Positive
Ratio of Investment in Treatment Facilities to Net Fixed Investment (7)	High	E.P.P. B.P.T. B.A.T.	2.5 2.5 2.5	245 0.0 13.7	8 8 8
Integration	Low		By-product	Moderate Forward; Low Backward	High
Chemical Complex	Isolated Plant		By-product	Complex	Isolated
Other Environmental Problems (Including OSHA)	Multiple		N.A.	Nominal	N.A.
Emotional Commitment	Indifference		Moderate	Medium	Low
Ownership	Multi-Industry Companies		Multi-Industry	Multi-Industry	Multi-Industry

## II. INDUSTRY CHARACTERIZATION--MAJOR STUDY PRODUCTS

### A. CALCIUM CARBIDE

#### 1. Summary

Calcium carbide is produced in the United States almost exclusively for conversion to acetylene gas. Acetylene is used primarily in the synthesis of various organic chemicals and plastics, although a significant amount is used as a fuel for welding and other metalwork.

Production of calcium carbide declined more than 50% by 1972 from a peak reached in the mid-1960's. The main reason for this decline has been the substitution of acetylene derived from hydrocarbons for that produced from calcium carbide for the manufacture of organic chemicals. Acetylene for chemical uses has also been largely replaced by other, less expensive, raw materials.

While the lower cost of shipping calcium carbide to industrial centers for conversion to fuel acetylene has favored this source over tanked, hydrocarbon-derived acetylene, more convenient and economical fuels (e.g., propane) have made significant inroads into the amount of acetylene used for metalworking.

The general trend of a declining market for calcium carbide is likely to continue as hydrocarbon-derived acetylene replaces carbide-derived acetylene for chemical use, and as other raw materials replace acetylene in both chemical and metalworking applications.

#### 2. Market Characterization

##### a. Size

U.S. production of calcium carbide reached a maximum of approximately 1.1 million tons per year in the period 1960 to 1965. Since U.S. foreign trade in this commodity has always been small in comparison to production, apparent annual consumption of calcium carbide was also at a level of about 1.1 million tons during this period, as is shown in Table 4. By 1972, production had fallen to less than half a million tons per year. Table 4 also indicates the low level of imports, which have ranged between 1% and 3% of consumption in recent years, and have come exclusively from Canada.

##### b. Growth

Calcium carbide producers have experienced a steady drop in demand for almost a decade. Annual market value data for calcium carbide production since 1950 are given in Table 5. While 1972 production, at

TABLE 4

### CALCIUM CARBIDE PRODUCTION, IMPORT/EXPORT, AND APPARENT CONSUMPTION (Thousands of Tons)

Year	Production	Imports	Exports <sup>1</sup>	Apparent Consumption <sup>2</sup>
1950	671	6	6	671
1955	875	2	4	873
1960	1,093	5	5	1,093
1961	1,042	5	6	1,041
1962	1,083	6	6	1,083
1963	1,109	7	6	1,110
1964	1,132	12	6	1,138
1965	1,098	11	-	1,109
1966	1,063	20	-	1,083
1967	912	8	-	920
1968	942	7	-	949
1969	856	18	-	874
1970	791	19	-	810
1971	625	20	-	645
1972	493	11	-	504

<sup>1</sup> Exports not reported separately after 1964.

<sup>2</sup> Apparent consumption: production and imports minus exports.

Source: U.S. Department of Commerce.

TABLE 5

## TOTAL MARKET VALUE OF CALCIUM CARBIDE PRODUCTION

Year	Production (Thousands of Tons)	Market Value (\$/Ton)	Total Market Value (\$MM)
1950	671	78	52.3
1955	875	94	82.3
1960	1,093	100	109.3
1961	1,042	99	103.5
1962	1,083	93	101.0
1963	1,109	95	104.9
1964	1,132	91	102.8
1965	1,098	89	97.7
1966	1,063	87	92.5
1967	912	94	85.7
1968	942	94	88.5
1969	856	78	66.8
1970	791	81	64.1
1971	625	90	56.3
1972	493	90 (est.)	44.4

Sources: U.S. Department of Commerce, and Contractor's estimates.

493,000 tons represented a 55% drop from 1960 production levels, price erosion has caused the total market value of calcium carbide production to drop 60% over the same period (from \$109 million to \$44 million).

## c. Uses

Although a small quantity of calcium carbide is consumed in such direct applications as the carburization of steel, desulfurization, and other foundry work, by far the largest use is in the production of acetylene. In the preferred "dry" process, water is added to calcium carbide to form acetylene and calcium hydroxide at the rate of 640 pounds of acetylene per ton of carbide. The "wet" process uses excess water, and produces by-product calcium hydroxide in a slurry which is 90% water.

Approximately 80% of the acetylene produced from calcium carbide is used as a raw material in the synthesis of organic chemicals and plastics by the chemical industry. The balance is used as a fuel in metalworking for welding, cutting, and scarfing. A summary of calcium carbide use, showing representative products produced by the chemical industry, is given in Table 6.

## d. Substitute Products

Until 1951, all of the acetylene produced in the United States was derived from calcium carbide. Since that time, acetylene has also been manufactured through the pyrolysis, or cracking, of hydrocarbons. This process produces several other important industrial chemicals as by-products, and has become increasingly competitive with the calcium carbide route to acetylene.

The advantage of calcium carbide as a source of acetylene is that the carbide can be shipped more economically than the heavy cylinders of compressed acetylene gas. Thus, for uses which are geographically removed from the production of hydrocarbon-derived acetylene, calcium carbide as a source of acetylene is less-susceptible to substitution. Even here, however, carbide acetylene faces competition from other fuels, such as propane or natural gas, and also from electric-arc welding.

In such direct applications as the carburization of steel, desulfurization, and use as a drying agent, calcium carbide also faces competition from a variety of products. In foundry work, various combinations of lime, coke, and magnesium can replace calcium carbide. Calcium sulfate is only one example among a variety of alternative drying agents which are available as substitutes for calcium carbide. These direct applications currently account for only about 3% of U.S. consumption.

## e. Geographic Consumption

Except for the relatively small amount of calcium carbide used to generate acetylene for metalworking, virtually all calcium carbide



TABLE 6

USE PATTERN OF CALCIUM CARBIDE BY APPLICATION<sup>1</sup>

<u>Calcium Carbide Converted to Acetylene</u>	97%
<u>Chemical Acetylene</u>	80%
Used in synthesis of organic chemicals (e.g., butadiene, allyl alcohol, vinyl ethers) and derived products such as neoprene, other plastics, and resins.	
<u>Fuel Acetylene</u>	17%
Used for welding, cutting and scarfing in metalwork, and for production of acetylene black.	
<u>Calcium Carbide for Direct Use</u>	3%
Includes use as a dehydrating agent and a reducing and desulfurizing agent in certain metallurgical processes.	
	100%

<sup>1</sup>This use pattern is typical of consumption in 1972. Chemical use of calcium carbide acetylene is rapidly becoming much less significant.

Sources: Kirk-Othmer, Encyclopedia of Chemical Technology; Shreve, Chemical Process Industries; and Contractor's estimates.

is consumed in the region in which it is produced. In fact, most carbide acetylene is generated either in the same plant as the carbide, or in an adjacent one. In 1972, nearly 85% of U.S. calcium carbide production capacity was located in Kentucky and Ohio, and with it, the bulk of calcium carbide consumption. Most of the remaining 15% of consumption occurs in major industrial metalworking cities such as Cleveland, Detroit, and Pittsburgh.

f. Captive Requirements

As indicated above, calcium carbide is most often used as a ready source of acetylene. Furthermore, the greatest portion of calcium carbide is consumed either in the same plant as it is produced, or at another plant owned by the same company. Although the most recent information on merchant shipments was given in 1965, it is apparent from these data that captive consumption was typically at a level of 75%. Data illustrating this relationship for the years 1962 through 1965 are given in Table 7. Although the trend in recent years has been away from captive use, as acetylene for chemical synthesis has been replaced by ethylene, propylene, and other less expensive raw materials, the bulk of calcium carbide production will be consumed captively throughout the 1970's.

3. Supply Characterizationa. Manufacturing Route

Calcium carbide is prepared from quicklime (calcium oxide) and coke (carbon) which are mixed together at approximately 2000° C. This temperature is achieved in an electric furnace using large amounts of electric power. In a typical run, 1900 pounds of quicklime, 1300 pounds of coke, and 3,000 kilowatt hours of electricity are required to produce one ton of calcium carbide. The product, tapped from the furnace as a liquid, is allowed to solidify and is then crushed to a convenient size for packing and handling. Calcium carbide for chemical acetylene often goes directly to an acetylene generator in the same plant.

An example of the overall process is shown in Figure 3 as a simplified schematic diagram. The source of quicklime is a high-grade limestone containing nearly 100% calcium carbonate. The limestone is heated in a kiln to produce quicklime, which is combined with coke, or another source of carbon such as anthracite, in the electric furnace. The large power requirements and high raw material shipping costs are important factors in determining plant location.

b. Producers

In 1972, calcium carbide was produced in seven plants by four different companies. As indicated in Table 8, three of these plants

**TABLE 7**  
**CAPTIVE VS. COMMERCIAL CONSUMPTION OF CALCIUM CARBIDE**  
(Thousands of Tons)

Year	Production	Consumption		
		Captive	Merchant <sup>1</sup>	Percent Captive
1962	1,083	815	268	75
1963	1,109	824	285	74
1964	1,132	891	241	79
1965	1,098	819	279	75

<sup>1</sup>Last reported separately in 1965.

Source: U.S. Department of Commerce.

**FIGURE 3**  
**SCHEMATIC FLOW DIAGRAM--PRODUCTION OF CALCIUM CARBIDE**

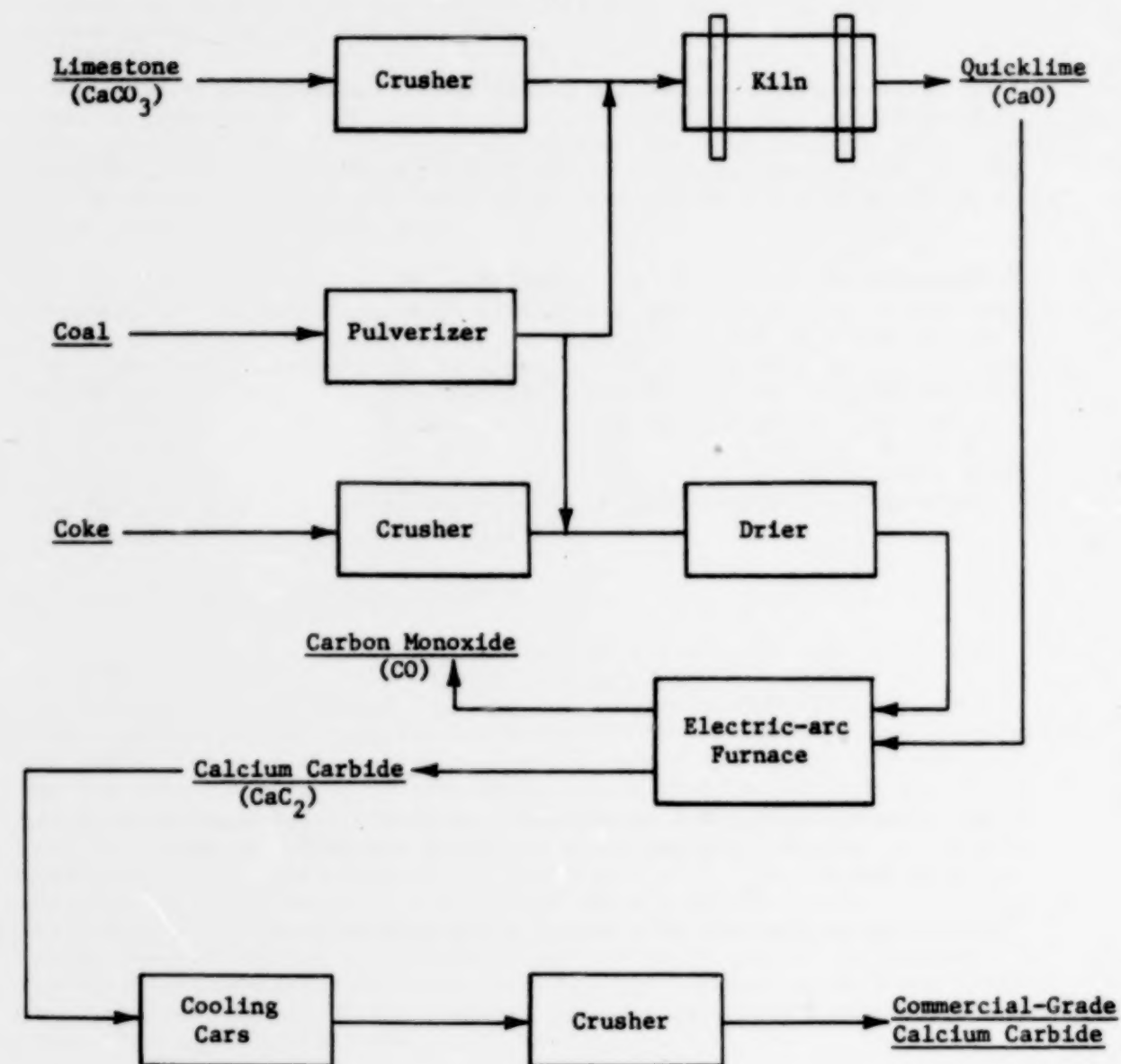


TABLE 8

CALCIUM CARBIDE PRODUCERS--LOCATION AND CAPACITY  
(Thousands of Tons)

<u>Producer</u>	<u>Location</u>	<u>Annual Capacity</u>
Airco, Inc. Airco Carbide Div. <sup>1</sup>	Calvert City, Ky. Louisville, Ky.	325 150
Midwest Carbide Corp.	Keokuk, Iowa Pryor, Okla.	30 50
Pacific Carbide & Alloys Co.	Portland, Ore.	20
Union Carbide Corp. <sup>2</sup> Chemicals & Plastics Div.	Ashtabula, Ohio Portland, Ore.	228 35
Total		838

<sup>1</sup>Manufacturing operations in Calvert City were discontinued early in 1973; the Louisville plant is to be phased out over the next several years.

<sup>2</sup>Operations at Portland were discontinued in mid-1973.

Sources: Trade journals, industry contacts.

were responsible for most (84%) of the 1972 annual production capacity of 838,000 tons. These were the Airco plants at Calvert City and Louisville, Kentucky, and the Union Carbide plant at Ashtabula, Ohio.

A decade ago, in 1960, there were twelve plants, with a combined capacity of 1,225,000 tons. The move to reduce capacity, which began in the early 1960's, has continued into 1973 with the announcement by Airco that operations would be discontinued at the Calvert City plant, and that the Louisville plant would be phased out by about 1980. The closing of Calvert City has reduced 1973 U.S. capacity by 39% to approximately 513,000 tons per year.

Existing calcium carbide plants may be classified as either large (annual capacity 150,000 tons or more), or small (annual capacity 50,000 tons or less), with four of the six plants operating in early 1973 classified as small. All of these plants are at least ten years old and some are much older. Airco's Calvert City plant had been operating about 20 years when it closed this year.

As stated earlier, approximately 75% of all calcium carbide produced is captively consumed. This gives some indication of the large degree of intra- and inter-company integration in the sale and use of this chemical commodity. As an example, the Airco plant at Calvert City, which was the largest calcium carbide plant in the world, shipped a small part of its output to the Airco plant in Louisville, and converted the rest to acetylene for local use. This local use included chemical synthesis at an adjacent Airco plant, and shipment of acetylene and derived products by pipeline to the plants of several other firms in the large Calvert City chemical complex.

c. Manufacturing Economics

A summary of estimated manufacturing costs for calcium carbide is given in Table 9. The data in this table are for a plant of 45,000 ton-per-year annual capacity, operating at 100% capacity. A plant of double this capacity would benefit from relatively small economies of scale, reducing manufacturing costs by about 5%, to \$81 per ton. On the other hand, a plant producing calcium carbide for fuel acetylene, as opposed to chemical acetylene, experiences manufacturing costs which may be from 5% to 6% higher than that shown in Table 9 due to quality requirements relating both to raw materials and to the manufacturing process itself. General, selling, and administrative expenses are estimated to be 5% of manufacturing costs. This brings total costs to about \$90 per ton for a 45,000 ton-per-year plant producing calcium carbide for conversion to chemical acetylene. Depending on plant size and intended end use of the product, total manufacturers' costs may vary from approximately \$85 to \$95 per ton.



TABLE 9

## ESTIMATED COST OF MANUFACTURING CALCIUM CARBIDE

Plant Capacity: 45,000 Tons/Yr (1-15,000 KVA furnace)  
 Fixed Investment: \$3,740,000

	Quantity/Ton	\$/Unit	\$/Ton
<u>Variable Costs</u>			
Quicklime	0.95 ton	18.75	17.81
Coke	0.65 ton	24.00	15.60
Carbon Electrodes	30 lb.	0.15	4.50
Operating Supplies			0.30
Power	2780 kwh	0.007	19.46
Water	32 M gal	0.02	0.64
			58.31
<u>Semi-Variable &amp; Fixed Costs</u>			
Operating Labor	9 men/shift	4.25/hr	7.45
Supervision	4 foremen	12,000/yr	1.07
	1 superintendent	17,000/yr	0.38
Maintenance	4½% of investment/yr		3.73
Labor Overhead	30% of operating labor and supervision		2.67
Plant Overhead	70% of operating labor and supervision		6.23
Depreciation <sup>1</sup>	6-2/3% of investment/yr		5.53
Local Taxes & Insurance	1½% of investment/yr		1.25
			28.31
Cost of Manufacture (Bulk)			86.62
Off Gas Credit <sup>2</sup>	3.14 MM Btu	0.35	(1.10)
Net Cost of Manufacture <sup>3</sup> (Bulk)			85.52

<sup>1</sup>For older plants depreciation may only cover items replaced and be about 20% of this amount.

<sup>2</sup>Credit valid only if carbon monoxide can be utilized as fuel at plant.

<sup>3</sup>Quality requirements make manufacturing costs about \$5/ton higher for manufacturers of calcium carbide for use in generation of fuel acetylene.

## 4. Supply/Demand Balance

Industry capacity for calcium carbide has gradually been reduced since the early 1960's. As of 1972, capacity had been reduced by 30%, while production had fallen by more than 50%. In the early 1960's, operating rates were typically close to 90% of capacity; in the early 1970's operating rates have generally been below 80%, and it is only the shut down of the largest plant in the industry (Calvert City) which has brought current capacity down to a level consistent with current demand.

In view of the continued replacement of carbide acetylene by hydrocarbon-derived acetylene, and replacement of acetylene for chemical use by less expensive raw materials, this trend towards reduction of excess capacity is likely to continue as demand is further reduced. Total production in the first two months of 1973, for example, was 20% below that of the same period in 1972.

## 5. Prices

Published prices for packaged and delivered calcium carbide have increased steadily from \$121 per ton in the early 1950's, to a level of \$171 per ton since 1963. A more realistic price for 1972 is the \$100 per ton, f.o.b. plant, quoted by industry sources. Some discounting occurs, and the average actual price received for calcium carbide shipments has been somewhat lower than this in recent years, as is shown in Table 10. In addition to discounting, and as indicated in the footnote for Table 10, the difference between actual and published prices also reflects packaging and freight charges. Packaging charges range from \$35 to \$45 per ton, and freight charges add approximately \$10 per ton locally and up to \$20 per ton for more distant shipments within a given region.

Information on 1972 actual prices is not yet available, but it appears that the declining trend was at least temporarily halted in 1971 when actual price increased approximately 10%, from \$81.00 to \$90.00 per ton. In any case, a comparison of manufacturer's total costs with actual prices received per ton of calcium carbide, indicates that U.S. producers of this chemical are currently operating at, or near, the break-even level.

TABLE 10

CALCIUM CARBIDE PRICES--PUBLISHED VS. ACTUAL  
(Dollars per Ton)

<u>Year</u>	<u>Published Price</u> <sup>1</sup>	<u>Actual Price</u> <sup>2</sup>
1950	121	78
1955	134	94
1960	149	100
1965	171	89
1970	171	81
1971	171	90
1972	171	N.A.

<sup>1</sup>Published prices include packaging and freight charges of ca. \$50/ton. Quoted 1972 price for bulk calcium carbide was \$100 per ton, f.o.b. plant.

<sup>2</sup>Actual Price: Total Value of Shipments/Tons Shipped.

Sources: Chemical Marketing Reporter, U.S. Department of Commerce, and Contractor's estimates.

B. SODIUM SULFATE1. Summary

Sodium sulfate is produced in the United States largely as a joint product with some other material, rather than for its own value. This joint-product characteristic, combined with a low price, has often led to a situation where the potential supply of sodium sulfate has exceeded demand. Uses have been developed to take advantage of the large, inexpensive supplies. As a result sodium sulfate has become an important material to several industries, and its low cost ultimately translates to lower product costs in those industries where it is used.

Sodium sulfate is used in the paper industry, by detergent manufacturers, and in the manufacture of glass and textiles. U.S. consumption has averaged 1.6 million tons over the last decade, and this level of use is likely to be characteristic of the foreseeable future.

2. Market Characterizationa. Size

U.S. production of sodium sulfate was approximately 1.36 million tons in 1972, down 8% from a record level of nearly 1.5 million tons in 1968. Total value of 1971 shipments was \$28 million.

Net imports of about 0.27 million tons in 1972 (equal to 20% of U.S. production) brought total 1972 U.S. apparent consumption to approximately 1.63 million tons. Belgium accounted for 48% of import dollar value, Canada 38%, and in descending order of importance, The Netherlands, East Germany, Sweden, West Germany, and Japan accounted for the remaining 14%.

Historical data for production, foreign trade, and apparent consumption are given in Table 11. In this table, and in Table 17. (giving price information) the data are presented for both high purity (anhydrous sodium sulfate), and lower purity (saltcake) grades of sodium sulfate. Most of this analysis will be in terms of aggregate data for both grades.

b. Growth

As Table 11 illustrates, both U.S. production and apparent consumption of sodium sulfate reached record levels in 1968. Between 1968 and 1972, production decreased 8% and apparent consumption



TABLE 11

## SODIUM SULFATE PRODUCTION, IMPORT/EXPORT, AND APPARENT CONSUMPTION

(Thousands of Tons--100% Na<sub>2</sub>SO<sub>4</sub>)

Year	Production, by Type <sup>1</sup>		Foreign Trade <sup>2</sup>		Apparent Consumption <sup>3</sup>
	Saltcake	Anhydrous Na <sub>2</sub> SO <sub>4</sub>	Imports	Exports	
1960	810	303	167	31	1249
1961	844	327	196	32	1335
1962	826	368	188	51	1331
1963	837	396	160	45	1348
1964	926	390	290	44	1562
1965	976	428	274	13	1665
1966	1,009	436	237	28	1654
1967	696	668	290	28	1626
1968	758	725	305	56	1732
1969	730	744	286	91	1669
1970	561	812	269	55	1587
1971	514	843	269	67	1559
1972	681	683	299	29	1634

<sup>1</sup> The large difference between pre-1967 and post-1966 production figures is due to a product classification change.

<sup>2</sup> Total for crude and refined sodium sulfate.

<sup>3</sup> Apparent Consumption: production plus imports minus exports.

Source: U.S. Department of Commerce. Data for 1972 are preliminary.

decreased 6%. Data for 1972 indicate that the downward trend has at least temporarily stopped. Production volume was up slightly (less than 1%) from 1971, and apparent consumption increased 5%.

While net imports were at a record level in 1972, and accounted for most of the 5% increase in apparent consumption between 1971 and 1972, it is difficult to discern a trend in imports over the past decade. From a low of 9% to a high of 20%, net imports have averaged 16% of U.S. production since 1962.

## c. Uses

An estimated use pattern for sodium sulfate is given in Table 12. By far the largest use (ca. 70%) is in the kraft, or sulfate, pulping process of the paper industry. Sodium sulfate is converted to sodium sulfide, and with sodium hydroxide and water, forms a digesting solution for wood chips. Techniques for recovering impure sodium sulfate (saltcake) from the digesting liquor are constantly being improved, but present losses average about 100 pounds of saltcake per ton of pulp. Purchased saltcake is used to replace that which is not currently recovered. Use in kraft pulping has remained relatively constant at about 1.1 million tons for the last ten years. Increasing requirements due to growing pulp demand have been offset by improved sodium sulfate recovery techniques.

The second largest use of sodium sulfate (ca. 18%) is in detergent formulations. A small amount is added to all detergents as part of the manufacturing process, but increasingly, manufacturers have been adding additional purchased sodium sulfate to their formulations. This additional sodium sulfate partly compensates for the loss of bulk and detergency brought about by decreased phosphate content. Sodium sulfate use in detergent formulation has doubled from about 150,000 tons in the early 1960's to about 300,000 tons in 1972.

Use in the manufacture of glass, in textile finishing, and other uses constitute the remainder (ca. 12%) of U.S. consumption of sodium sulfate. In glass manufacture, sodium sulfate speeds the melting of the raw material charge, improves the working properties of high-silica glass, and, when carbon is added, forms sulfur dioxide gas. The sulfur dioxide bubbles have a "fining" effect, removing other gas bubbles as they move toward the surface of the molten glass.

Use of sodium sulfate in glass manufacture has decreased slightly over the past decade due to restrictions on the sulfur dioxide content of stack gases. Manufacturers are being forced to cut down on the amount of sodium sulfate in each batch of glass and to install scrubbing units which will allow recycling of sodium sulfate. Current consumption is about 140,000 tons per year.

In textile manufacture, sodium sulfate finds use in the finishing operation. The primary use is dye standardization; that is,

**TABLE 12**  
**USE PATTERN OF SODIUM SULFATE BY APPLICATION**

Kraft (Sulfate) Paper Process Used with sodium sulfide and sodium hydroxide in the pulping-bleaching operation.	70%
Detergents Sodium sulfate is used in detergents to improve detergency and contribute bulk density to the formulation.	18%
Glass, Textile, and Other In approximate order of importance, sodium sulfate is used in "fining" glass, standardizing textile dyes, manufacturing cellulose sponges, as a cleaning and metal pickling agent, in mineral feed supplements, and in photography.	12%
	100%

Sources: Kirk-Othmer, Encyclopedia of Chemical Technology; Shreve, Chemical Process Industries; and Contractor's estimates.

dilution of the dye to a standard potency. Sodium sulfate is also added to the dye bath to level, or control, the color. Consumption of sodium sulfate for textile applications has remained fairly constant at an estimated 50,000 tons annually over the past several years.

Finally, several thousand tons per year of sodium sulfate find application in such uses as cellulose sponge manufacture, mineral feed supplements, cleansing agents, photography, and as a chemical catalyst.

#### d. Substitute Products

In applications which account for the bulk of U.S. sodium sulfate consumption, other products could be substituted with relative ease. The major consequence of such substitution would probably be increased manufacturing and product costs.

In kraft pulping operations, sodium sulfate is employed as the most economical source of make-up sodium and sulfur values. Other, more-expensive sources (e.g., sodium carbonate or caustic soda) could be substituted for the purchased saltcake, or "synthetic saltcake" may be manufactured by oxidizing a mixture of soda ash (sodium carbonate) and sulfur. Furthermore, the newer pulp mills will generate most, or all, of their saltcake requirements internally as a by-product of on-site chlorine dioxide bleach production. The only problem here is that sodium values must still be purchased outside, and high prices for sodium hydroxide or sodium carbonate can make this source of saltcake less attractive than purchased saltcake.

Increasing use of sodium sulfate in detergent formulation is, itself, the result of a substitution. Sodium sulfate, as an inexpensive electrolyte, serves to replace some of the lost detergency and bulk to detergents with reduced phosphate content.

#### e. Geographic Consumption

An estimated geographic use pattern for sodium sulfate is given in Table 13. More than 60% of sodium sulfate demand is in the U.S. south, and approximately 90% of this demand is attributable to the kraft pulping industry.

Approximately 16% of U.S. sodium sulfate demand is in the north-central--Great Lakes region. The primary use in this region (ca. 60%) is in detergent formulation, with kraft pulping operations accounting for most of the remaining consumption.

The U.S. west and northwest require an estimated 14% of annual U.S. sodium sulfate supply. Kraft mills account for most (ca. 75%) of this regional demand; detergent formulation and other uses make up the rest.

In the U.S. northeast, it is estimated that half of the 7% regional consumption is for detergent formulations; most of the remaining half is split between kraft pulping and glass manufacture.

TABLE 13  
GEOGRAPHIC USE PATTERN OF SODIUM SULFATE

South Approximately 90% - kraft pulping, 10% other.	63%
North Central - Great Lakes Approximately 60% - detergent formula- tion, 25% kraft pulping, 15% other.	16%
West and Northwest Approximately 75% - kraft pulping, 15% detergent formulation, 10% other.	14%
Northeast Approximately 50% - detergent formula- tion, 20% - kraft pulping, 20% glass fining, 10% other.	7%
	<hr/> 100%

Source: Contractor's estimates.

f. Captive Requirements

Production of sodium sulfate for captive use by producing companies is insignificant in the U.S. Nearly 90% of U.S. production is as by-product or co-product sodium sulfate. The small amount produced as primary product is produced for sale to end users. Table 14 shows a comparison of sodium sulfate production and shipments for the years 1962-1972. Shipments have averaged 99% of production over the last decade.

Production of by-product sodium sulfate during chlorine dioxide bleach manufacture at pulp mills, is the only significant case where by-product sodium sulfate is used in another operation by the same company.

g. Other Market Characteristics

Most of the sodium sulfate produced in the U.S. sells for about \$20 per ton, with price as the main basis for competition. In this price range, freight costs become a significant consideration in marketing and distribution of the product. Local shipment may cost up to \$15 per ton, and long distance shipping rates may be \$24 per ton and more. These rates are relatively high compared to transatlantic bulk shipping rates of about \$7 per ton, and allow foreign producers to compete effectively with U.S. companies located on the Atlantic coast.

Within the U.S., the relatively high freight costs cause local demand to be highly dependent on the proximity of sodium sulfate supply. Substitution may occur when freight-equalized costs of another product make its use more economical. An example is caustic soda as a source of sodium values for kraft pulping operations.

3. Supply Characterization

a. Manufacturing Routes

Sodium sulfate has rarely been produced in quantity for its own sake. A summary of sodium sulfate production by process, from 1964 to 1971, is given in Table 15. Only about one-third of the production classified as "natural" is recovered solely for sodium sulfate value, and in 1972, approximately 90% of U.S. production could be classified as by-product or co-product sodium sulfate.

By-product sodium sulfate is defined as sodium sulfate formed in a process which produces one or more other products of significantly higher value. These processes include manufacture of rayon and cellophane, lithium and strontium processing, and the chemical synthesis of sodium bichromate and resorcinol.

Co-product sodium sulfate is formed in a process which concurrently produces products having a value comparable to that of sodium



TABLE 14

CAPTIVE VS. COMMERCIAL CONSUMPTION OF SODIUM SULFATE  
(Thousands of Tons)

<u>Year</u>	<u>Production</u>	<u>Shipments</u> <sup>1</sup>
1962	1,194	1,170
1963	1,233	1,226
1964	1,316	1,303
1965	1,404	1,364
1966	1,445	1,398
1967	1,364	1,384
1968	1,483	1,469
1969	1,475	1,439
1970	1,373	1,386
1971	1,356	1,377
1972	1,364	- -

<sup>1</sup> Including interplant transfers.

Source: Current Industrial Reports, U.S. Department of Commerce.

Table 15

PRODUCTION OF SODIUM SULFATE BY PROCESS  
(Thousands of Tons)

<u>Year</u>	<u>Mannheim Furnace</u>	<u>Polymer By-Product</u>	<u>Sodium Dichromate and Other</u>	<u>Natural</u>	<u>Total</u>
1964	214	356	201	544	1,315
1965	224	382	190	608	1,404
1966	228	387	217	613	1,445
1967	196	346	228	594	1,364
1968	165	404	254	660	1,483
1969	181	388	282	624	1,475
1970	177	354	278	564	1,373
1971	162	362	210	622	1,356

Source: U.S. Department of Commerce.

sulfate. Examples of such processes are the Mannheim and Hargreaves processes for producing hydrochloric acid, and the recovery of sodium sulfate from natural brines and salts which contain a variety of inorganics of similar value.

One producer, with about 10% of U.S. capacity, has plants which sell sodium sulfate recovered from natural brines as their sole source of revenue. This is the only significant case in which sodium sulfate is produced as a primary product.

Methods for sodium sulfate production may be divided into three categories: recovery from natural sources, production as a by-product of rayon and cellophane manufacture, and production accompanying the synthesis of various chemicals.

Recovery from natural brines accounts for about half of U.S. sodium sulfate production. Figure 4 illustrates, in flow chart form, a typical process for recovery of both anhydrous sodium sulfate and Glauber's salt, a hydrated form of sodium sulfate. The natural brine, containing dissolved sodium sulfate and other inorganics, is pumped into a natural salt deposit to reduce the solubility of sodium sulfate. When the saturated solution is cooled, Glauber's salt precipitates. The mixture is filtered, and the hydrated sodium sulfate is collected for direct sale or for further processing to anhydrous sodium sulfate.

Production of sodium sulfate as a by-product of viscose rayon or cellophane production is responsible for about 30% of U.S. sodium sulfate capacity. Figure 5 is a schematic diagram for production of sodium sulfate as a rayon by-product. The sodium sulfate is formed in a spinning bath when the basic viscose rayon dope is forced through the fine holes of a spinneret into a solution containing sulfuric acid. Sodium sulfate is produced at a rate of about 1.2 pounds per pound of rayon or cellophane. The spinning bath must be refreshed periodically by removing the sodium sulfate which has formed and replenishing the sulfuric acid.

The production of certain industrial chemicals results in the formation of sodium sulfate as a natural result of the process used. Approximately 20% of U.S. sodium sulfate capacity is of this type. Figure 6 is a simple flow diagram for the Mannheim hydrochloric acid process. Salt (sodium chloride) and sulfuric acid are heated together to form hydrogen chloride and crude sodium sulfate. The crude sodium sulfate may be further refined or converted to Glauber's salt depending on relative demand for the two products.

Other examples in this third category of sodium sulfate production include the Hargreaves process for hydrochloric acid, formation with sodium bichromate when sodium chromate is treated with sulfuric acid, and production accompanying the synthesis of phenol and resorcinol.

#### b. Producers

In 1972 there were 22 companies producing sodium sulfate in 32 locations. These companies, plant locations and capacities, and

FIGURE 4

#### RECOVERY OF SODIUM SULFATE FROM NATURAL BRINES

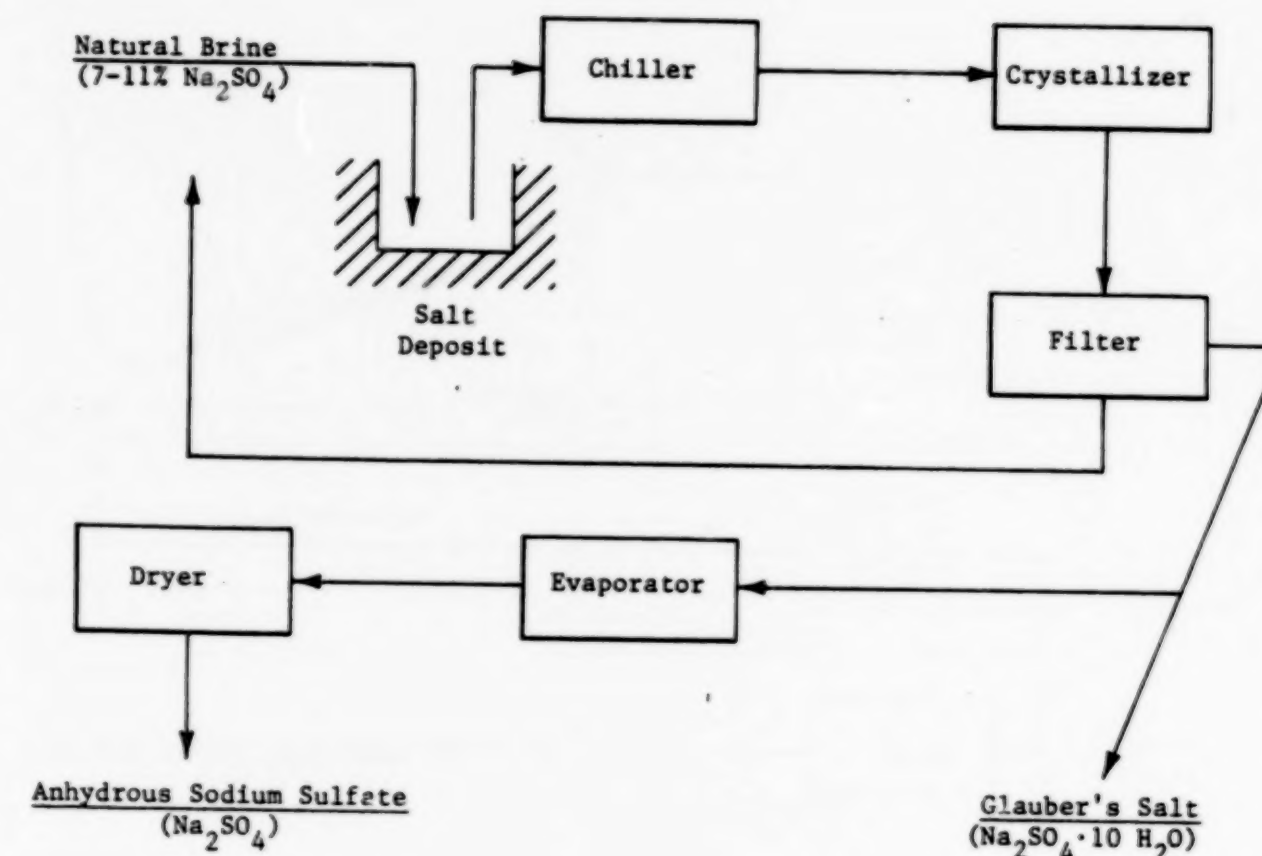


FIGURE 5

PRODUCTION OF SODIUM SULFATE IN VISCOSE RAYON PROCESS

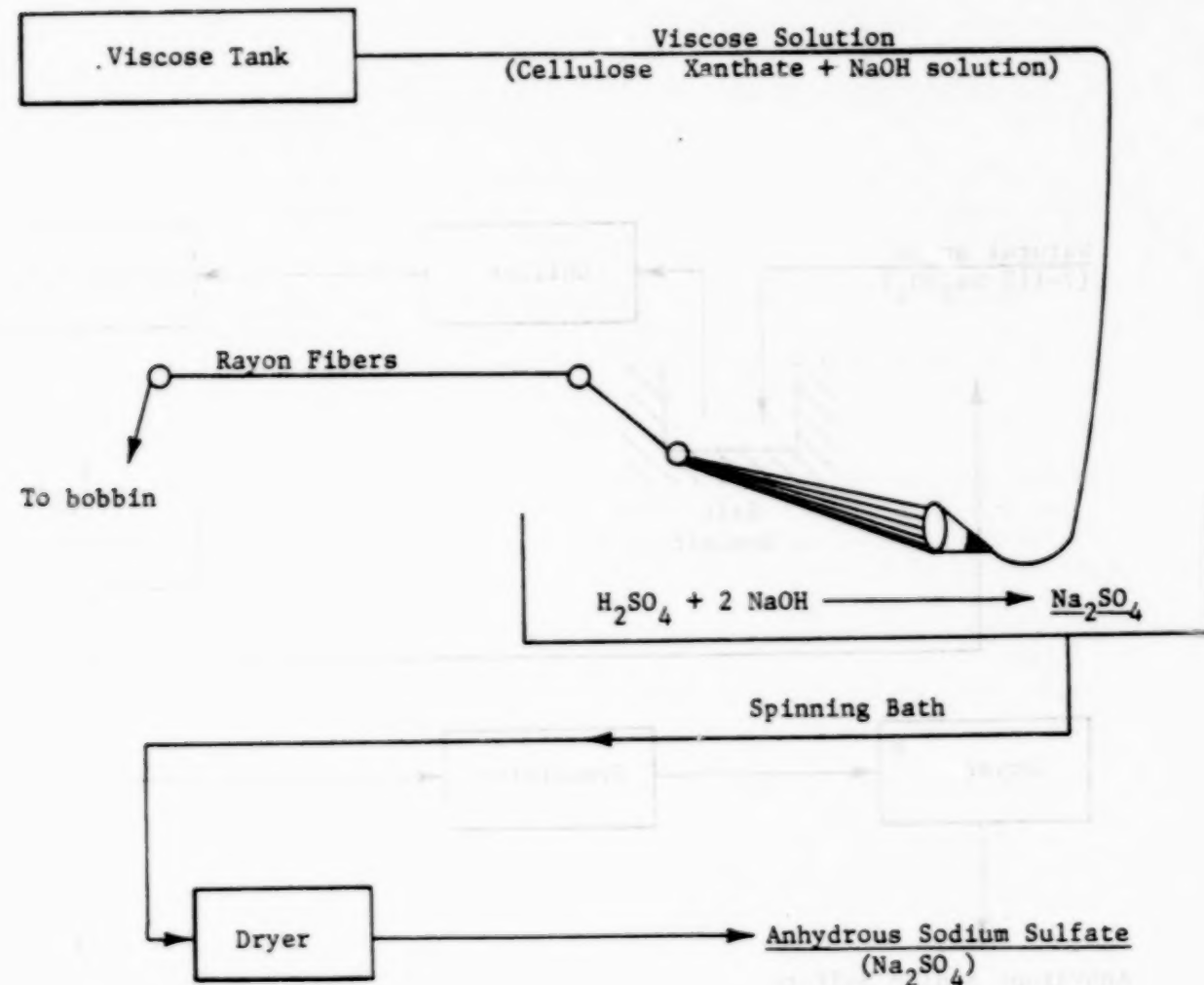
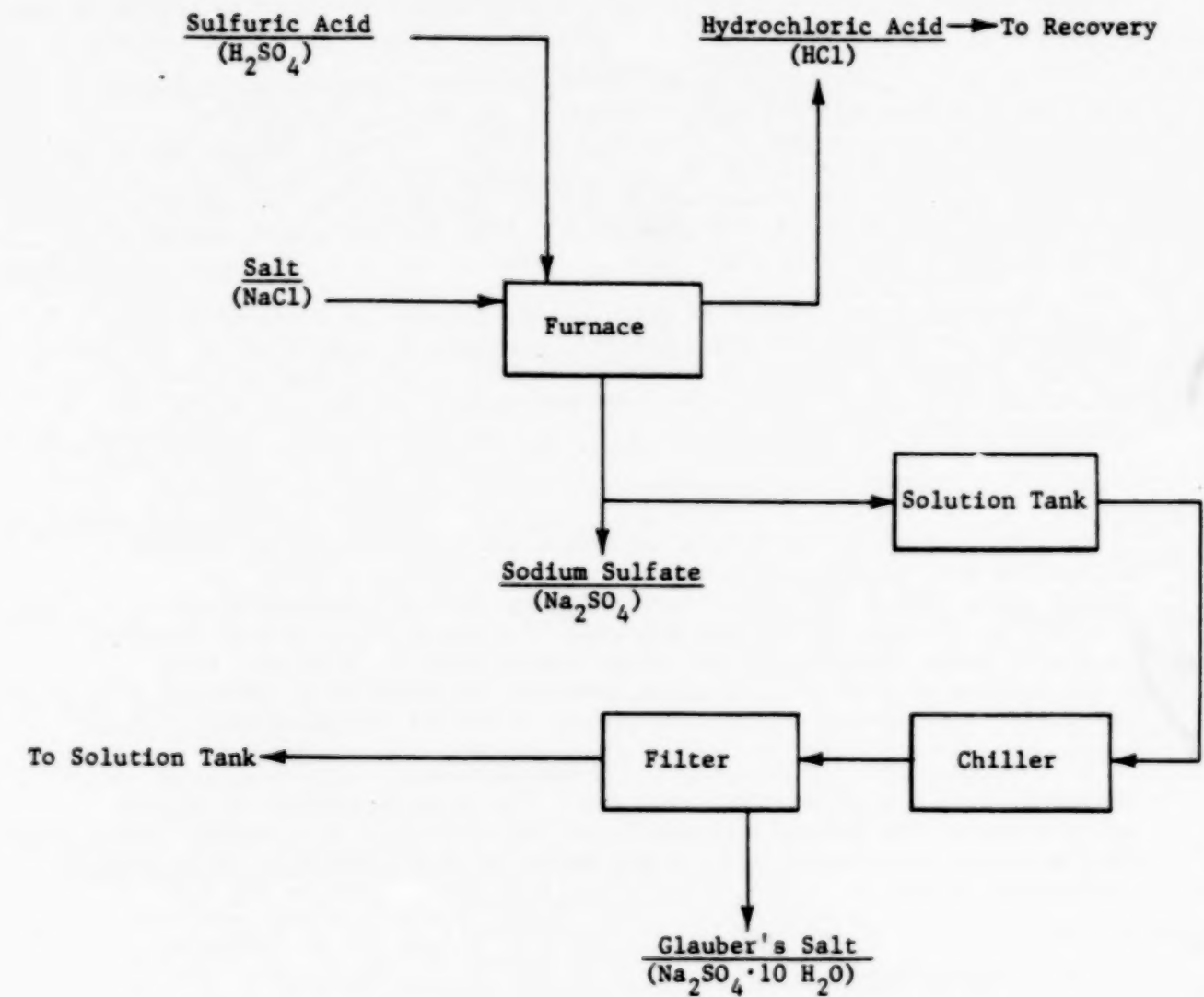


FIGURE 6

PRODUCTION OF SODIUM SULFATE IN THE MANNHEIM PROCESS





processes involved are given in Table 16. The five major producers accounted for 70% of 1972 U.S. capacity. Seven companies (10 plants) produce sodium sulfate from natural sources. Only one of these companies has facilities (2 plants) which produce sodium sulfate as their sole source of operating revenue. The others produce it as either a by-product or co-product along with other inorganics.

Five companies (11 plants) produce sodium sulfate as a by-product of rayon or cellophane manufacture, and ten companies (11 plants) produce sodium sulfate as a by-product or co-product of chemical synthesis operations.

Seven plants having approximately 100,000 tons-per-year capacity each, were responsible for 60% of 1972 U.S. capacity, and would be classified as large producers of sodium sulfate. Fifteen plants, of 25,000 tons-per-year capacity or less, accounted for 12% of 1972 U.S. capacity, and would be classified as small. The remaining ten plants, with capacities between 25,000 and 100,000 tons per year each, accounted for 28% of 1972 U.S. capacity.

The base materials from which sodium sulfate is produced as a by-product are long-established chemical commodities. It is therefore not surprising that many of the plants producing sodium sulfate are fairly old. Most plants have been operating at least ten years; some nearly twenty years.

#### c. Manufacturing Economics

Raw materials for sodium sulfate production are either natural brines and salt deposits or sodium alkalis and sulfuric acid. In either case, nearly all of the manufacturing cost is represented by separation, drying, and packaging costs. In the case of natural sources, depletion costs must be covered; where sodium sulfate is formed as a joint product of some manufacturing process, raw material costs are often allocated to each product according to its relative value.

We understand that water pollution abatement costs have been developed only for chrome saltcake, i.e., that sodium sulfate produced as by-product from sodium bichromate manufacture. For that reason, our sodium sulfate manufacturing cost estimates are included with the sodium bichromate costs.

#### 4. Supply/Demand Balance

Sodium sulfate has had an inverse relationship from that most often associated with the law of supply and demand. With nearly 90% of sodium sulfate production resulting from processes in which it is a by-product or co-product of some other material, and with both a low price and low profit margin, demand for this product has traditionally followed supply.

TABLE 16

#### SODIUM SULFATE PRODUCERS -- LOCATION AND CAPACITY

(Thousands of Tons)

Producer	Location	Annual Capacity	Process
Akzona Inc.			
American Enka Co., div.	Enka, N.C.	20	Polymer by-product
	Lowland, Tenn.	36	Polymer by-product
Allied Chem. Corp.			
Industrial Chems. Div.	Baltimore, Md.	50	Bichromate by-product
American Cyanamide Co.			
Indust. Chems. & Plastics Div.	Ft. Worth, Tex.	13	Catalyst by-product
IRC Fibers Co., subsid.	Painesville, Ohio	33	Polymer by-product
Chem. Met Corp.	Chicago, Ill.	--	
Climax Chem. Co.	Monument, N.M.	36	Mannheim furnace (HCl by-product)
Courtaulds North America, Inc.	Le Moyne, Ala.	25	Polymer by-product
El Paso Natural Gas Co.			
Beaunit Corp, subsid.			
Beaunit Fibers Div.	Elizabethton, Tenn.	25	Polymer by-product
FMC Corp.			
American Viscose Div.	Fredricksburg, Va. Fort Royal, Va. Lewistown, Pa. Marcus Hook, Pa. Nitro, W. Va. Parkersburg, W.Va.	275	Polymer by-product
Great Salt Lake Minerals & Chems. Corp.	Ogden, Utah	150	Natural; co-product
Green Bay Packaging, Inc.	Green Bay, Wisc.	--	By-product

TABLE 16 (Continued)

Producer	Location	Annual Capacity	Process
Gulf Resources & Chem. Corp. Lithium Corp. of America - Inc., subsid.	Bessemer City, N.C.	18	By-product
Hercules, Inc. Coatings & Specialty Products Dept.	Glens Falls, N.Y. } Hopewell, Va.	20	Bichromate by-product Polymer by-product
Kerr-McGee Corp. Kerr-McGee Chem. Corp. subsid.	Trona, Calif.	250	Natural, co-product
Koppers Co., Inc. Organic Materials Div.	Petrolia, Pa	15	Resorcinol by-product
Morton-Norwich Products, Inc. Morton Chem. Co. div.	Weeks Island, La.	120	Hargreaves furnace (HCl by-product)
Nalco Chem. Co. Industrial Div.	Chicago, Ill.	10	By-product
Ozark-Mahoning Co.	Brownfield, Tex. } Seagraves, Tex.	185	Natural, sole product Natural, sole product
Pratt Sodium Co.	Casper, Wyo.	2	Natural, by-product
Reichhold Chems., Inc.	Tuscaloosa, Ala.	--	Phenol by-product
Stauffer Chem. Co. Indust. Chem. Div.	San Francisco, Calif. West End, Calif.	228	Boric acid co-product Natural
U.S. Borax & Chem. Corp.	Boron, Calif. } Wilmington, Calif.	44	Boric acid co-product Boric acid co-product

Total: 1,555

Sources: Trade journals, industry reports.

With this type of relationship, there is often a time lag between increased supply and the development of new applications for the product. While supply often exceeds demand, the reverse is rarely true.

Evidence of this relationship of demand following supply is seen in the use pattern of sodium sulfate. From a technological point of view, very few uses of sodium sulfate result from unique chemical or physical properties of the compound. Rather, because of its relatively low price, sodium sulfate is often used wherever its chemical or physical properties allow its substitution in place of a more expensive material.

Substitution of sodium sulfate for higher cost materials wherever possible is a healthy economic practice, and does not detract from the importance of this chemical to both manufacturers and consumers. Even so, an excess of supply over demand is likely in the future, as water pollution abatement guidelines become more stringent. More rigorous water quality standards will have a dual effect: increasing recovery of by-product sodium sulfate, and decreasing consumption of sodium sulfate by kraft pulping mills and detergent manufacturers. Rayon and cellophane manufacturers, for example, currently recover only about one-third of the sodium sulfate produced by the industry. Kraft pulping mills, on the other hand, experienced sodium sulfate "losses" (in plant effluent) of about 250 pounds per ton of pulp in 1950, had reduced these losses to approximately 100 pounds per ton by 1972, and may be forced to reduce these losses by an additional 50% in the next decade. This lower demand as a result of kraft pulping effluent guidelines is in addition to reduced demand due to technical changes in bleaching and pulping operations.

In view of the joint-product nature of most U.S. sodium sulfate production, capacity figures are less meaningful for this chemical than for most others. Reported capacity is often much lower than theoretical capacity, and depends on the degree of commitment to recovering the sodium sulfate produced. Nevertheless, in terms of reported capacity, production of sodium sulfate has varied from 75% of capacity in 1964, to 100% in 1968. Production in 1972 represented approximately 90% of reported capacity.

On a regional basis, the U.S. south, northcentral, and northeast are net consumers of sodium sulfate, while the west and northwest are net producers. European sources supplement supplies to the U.S. south, and Canadian sources provide additional sodium sulfate to northern U.S. markets.

#### 5. Prices

Published and actual prices of sodium sulfate for representative years since 1950 are given in Table 17. The published price for lower purity sodium sulfate (saltcake) has been \$28 per ton since 1955. Actual prices for this grade have varied erratically in a narrow range from \$20 to \$22 per ton, indicating an average discount of 25%.



TABLE 17

## SODIUM SULFATE PRICES -- PUBLISHED VS. ACTUAL

(Dollars per Short Ton)

Year	Published Price <sup>1</sup>		Actual Price <sup>2</sup>	
	Lower Purity	High Purity	Lower Purity	High Purity
1950	22	40	12	17
1955	28	52	22	27
1960	28	54	22	29
1965	28	56	21	27
1970	28	48	20	21
1971	28	43	21	20
1972	28	--	--	--

<sup>1</sup> Published prices bulk, works, 100% Na<sub>2</sub>SO<sub>4</sub> basis for lower purity; bags, carlots, delivered East for high purity Na<sub>2</sub>SO<sub>4</sub>.

<sup>2</sup> Actual price: Value of Shipments/tons shipped.

Sources: Chemical Marketing Reporter, U.S. Department of Commerce, and Contractor's estimates.

Prices for higher grades of sodium sulfate are more difficult to characterize due to the number of different grades in this category, but it appears that considerable discounting occurs, and that the average price commanded by higher grades has declined in recent years. In 1971, the average price of high-purity sodium sulfate was below that of the lower quality grade. This unusual situation is most likely the result of increased recovery of this high-purity grade from rayon manufacture.

## C. TITANIUM DIOXIDE

## 1. Summary

In 1972, U.S. titanium dioxide (TiO<sub>2</sub>) consumption, including imports, was approximately 787,000 tons, with paint, paper and plastics applications accounting for nearly 80% of the total. Market demand growth in recent years has been at a 3% to 4% rate and is expected to continue at least at that rate through 1975. Imports remain a relatively small proportion (10%) of sales and are generally used only in non-critical, lower-cost applications.

While TiO<sub>2</sub> is sold in volumes comparable to those of some commodities, it is marketed more as a specialty chemical rather than a commodity. Producers' marketing efforts in recent years have been centered around grade improvement, quality control, and customer-oriented technical service. Depending on particular product expertise, individual producers frequently are strong in one market segment, such as paper, but do not fare as well in another--paint, for instance.

Current list prices are 28.5¢ per pound for rutile grades, 24¢ per pound for paper grade, and, at these prices, TiO<sub>2</sub> frequently is one of the more expensive raw materials in its end-use application. List prices have historically been stable or slowly rising, with the industry generally attempting to move as a whole to a given new price level. A long-established 1¢ per pound price differential between anatase and rutile grades disappeared in 1971 and both grades are currently offered at the same list price. Due mostly to overcapacity problems, the industry has been plagued with substantial price discounts which forced several major producers to operate at a loss in the 1970-71 period. Prices have firmed in recent months.

TiO<sub>2</sub> is manufactured by either of two processes--sulfate and chloride. Current domestic manufacturing capacity is about 817,000 tons, approximately 54% of which is sulfate. The sulfate process is older and employs sulfuric acid to separate and recover TiO<sub>2</sub> from ilmenite, the principal raw material used in this manufacturing route. The sulfate process has the disadvantage of producing a large amount of potential pollutants in the form of spent sulfuric acid and ferrous sulfates (copperas). Depending on processing steps employed, both anatase and rutile, the two chemical forms of TiO<sub>2</sub>, can be produced. Estimated current manufacturing cost for pigment via the sulfate process is approximately 21¢ per pound, including pigment finishing steps.

The alternate method of production, and the one employed in every TiO<sub>2</sub> plant built since 1956, is the chloride process. In this process,

chlorine is reacted at high temperature with the raw ore, generally rutile, a high TiO<sub>2</sub>-content material. TiO<sub>2</sub> is recovered later in the process through further chemical treatment, and approximately 90% of the chlorine is recovered for reuse. Due to higher quality ore and reactant recycling, the chloride process produces far less pollutant by-product than the sulfate process. Although rutile pigment has been the sole product from the chloride process in the past, Du Pont will begin production of both anatase and rutile grades upon conversion of its Edgemoor, Delaware, plant to 100% chloride production in 1974. Chloride pigment has more uniformly consistent particle size, hence it offers greater hiding power and is used preferentially in certain critical applications such as automotive paint. Current chloride process manufacturing cost is estimated at nearly 23¢ per pound.

TiO<sub>2</sub> for commercial production is obtained from four principal sources--ilmenite, rutile, leucoxene, and slag. Ilmenite contains approximately 50% TiO<sub>2</sub>, is mined virtually worldwide, and is the basic raw material for the sulfate process and for Du Pont's chloride process plants. World supply is plentiful with present production of nearly three million short tons per year. U.S. production is approximately 700,000 short tons. Rutile, containing 95+% TiO<sub>2</sub>, is the raw ore for most chloride production and is found almost exclusively in Australia. World supplies are believed to be limited to 20-25 years at present production rates of over 400,000 long tons per year. No rutile is mined in the U.S.

Leucoxene and titanium slag, used in sulfate production, are relatively minor sources of TiO<sub>2</sub> worldwide, although over 100,000 tons of Canadian slag are imported into the U.S. every year.

2. Market Characterization

a. Market Size and Growth

U.S. market demand for TiO<sub>2</sub> pigments in 1972 was approximately 787,000 short tons, valued at nearly \$433 million on a delivered basis. Table 18 shows the recent history of TiO<sub>2</sub> production, trade and shipments data. Since 1965, overall market growth has been at an annual rate of 3% to 4%, although certain individual end-use segments, such as plastics, have grown considerably faster.

Exports of TiO<sub>2</sub> have remained quite small, less than 2% to 3% of domestic production, and have actually declined somewhat in recent years. Imports, on the other hand, have ranged in recent years from 5% to 10% of total apparent consumption, although 1972 saw a large jump to 86,400 tons, or 11% of apparent consumption. Imports will probably continue at present percentage levels for the foreseeable future.

b. Product Uses

Table 19 identifies the major end uses and recent consumption history for TiO<sub>2</sub> pigments. Paint and coatings applications, currently

TABLE 18  
TiO<sub>2</sub> APPARENT CONSUMPTION AND INDUSTRY SHIPMENTS  
(Thousands of Tons)

Year	Production	Imports	Exports	Stocks	Apparent Consumption	Total Shipments	Commercial Shipments
1965	576.7	49.6	17.0	101.7	606.3	573.0	524.5
1966	594.5	48.0	15.0	98.5	630.7	593.3	545.4
1967	589.4	46.8	14.0	103.3	617.4	582.3	542.5
1968	623.7	53.3	15.0	94.2	671.1	632.1	564.4
1969	664.3	53.2	14.0	100.8	684.3	654.5	590.1
1970	655.3	60.2	15.0	106.9	691.4	643.7	560.9
1971	677.8	42.8	14.0	89.7	723.6	684.7	581.2
1972	687.3	86.4	10.0	66.3	787.1	-----	-----

Sources: U.S. Department of Commerce "Current Industrial Reports" and Tariff Commission trade data.

**TABLE 19**  
**TiO<sub>2</sub> MARKET CONSUMPTION**  
(Thousands of Tons)

	<u>1965</u>	<u>1970</u>	<u>1972</u>
Paint and Coatings	345	375	390
Paper	110	147	158
Plastics	27	59	78
Rubber	31	35	35
Floor Covering	29	30	30
Printing Ink	12	18	20
Ceramics	10	17	21
Synthetic Fibers	6	10	10
Roofing Granules	4	5	5
Other	<u>26</u>	<u>34</u>	<u>40</u>
Total	600	730	787

Source: Contractor's estimates.

accounting for 50% of total consumption, constitute the major use for TiO<sub>2</sub>. Two other end uses, paper and plastics, have grown rapidly in recent years, and in 1972, accounted for an additional 30% of TiO<sub>2</sub> consumption.

#### (1) Paint and Coatings

The paint and coatings industry is comprised of two basic segments--trade and industrial--with trade sales accounting for about 60% or 235,000 tons of TiO<sub>2</sub> consumption in the paint industry. Due to its interior hiding power and dispersibility (relative to rutile), anatase grade TiO<sub>2</sub> is rarely used, exceptions being low-cost applications such as highway paint. Within rutile grades, chloride process pigments account for about 60%, or 240,000 tons of paint pigment.

Sulfate producers have worked hard in recent years to eliminate previous performance deficiencies of sulfate rutile grades, and for many trade sales applications, such as interior wall paint and exterior house paint, sulfate and chloride grades are interchangeable. In industrial applications, the chloride process pigments, with Du Pont's R-900 series grades as the industry standards, enjoy clear superiority.

A critical factor in selling TiO<sub>2</sub> to the paint industry is a customer-oriented marketing effort. With TiO<sub>2</sub> pigment cost typically comprising 10% to 25% of paint selling price, paint manufacturers demand quality technical service and grade development to meet ongoing paint application needs. Imported TiO<sub>2</sub> has fared poorly in the paint industry due to lack of good customer service.

#### (2) Paper

1972 TiO<sub>2</sub> sales to the paper industry were about 158,000 tons and sales to the industry have been growing at 6% per year. Anatase grade pigments, because of their lower cost, account for about 70%, or 110,000 tons, of pigment sales. (TiO<sub>2</sub> frequently competes with 10 to 12¢ per pound clays for whitening and opacity filler applications; hence cost is a critical factor, and imported anatase grades have made their most successful penetration in this market.)

There are two main application areas within the paper industry--beater and coatings. Beater applications call for pigment addition directly to the paper pulp, and there is much grade and supplier interchangeability. A recent trend in beater use has been an increased TiO<sub>2</sub> requirement as paper sheet has become thinner while retaining opacity. In the coating area, use of rutile grade TiO<sub>2</sub> has been increasing, and there is less grade interchangeability than in beater use.

#### (3) Plastics

The fastest growing market segment for TiO<sub>2</sub> is plastics, with 1972 consumption of about 78,000 tons and a recent growth rate of nearly



17% a year. Major application areas included polyethylene injection molding and film production, polystyrene extrusions, and vinyl extrusions, such as outdoor siding and moldings. Product performance is the critical factor in plastics use, and rutile accounts for over 95% of  $TiO_2$  sales. Rutile pigment, both chloride and sulfate, is superior to anatase in dispersion and resistance to discoloration and weathering. Technical service is very important, and it is common for producer and user to work together in developing new applications. Imported  $TiO_2$ , again due to lack of customer service, has made little headway in this market.

#### (4) Other Applications

The remaining applications shown in Table 19 make up the remaining 161,000 tons of  $TiO_2$  consumed in 1972. Individual applications and their consumption relative to the total are as follows: rubber, 4%; floor covering, 4%; printing ink, 2.6%; ceramics, 2.6%; synthetic fibers, 1%; roofing granules, 0.5%.

#### c. Substitute Products

$TiO_2$  use presently is threatened by substitute products in only one market segment, paper. There  $TiO_2$  enjoys the advantage of being an effective opacifier, but it is at a cost disadvantage to alumina and silica clays, some of which offer nearly equivalent brightness as  $TiO_2$ . In the paint industry,  $TiO_2$  is by far the most effective white pigment in terms of hiding power, a key to the trend toward one-coat paint applications. While pigment research is extensive, no equally effective substitute has been found. In plastics and rubber,  $TiO_2$  offers the best combination of white pigment cost, dispersion, and resistance to discoloration. In other product application areas, no substitute products represent serious threats to  $TiO_2$ 's present position.

#### d. Captive Consumption

The major captive use of  $TiO_2$  pigment is in the paint industry, where three of the top six  $TiO_2$  consumers have their own pigment plants. Table 20 details captive  $TiO_2$  consumption and shows the rise in captive use as a percentage of apparent consumption from 8% in 1965 to 14% in 1971. Sherwin-Williams, Du Pont, Glidden-Durkee, and NL Industries are the major captive users, and it is believed that these companies account for virtually all of the captively-consumed  $TiO_2$  pigment.

### 3. Supply

#### a. Manufacturing Processes

Two commercial processes are presently employed to produce  $TiO_2$  pigments--the sulfate process and the chloride process. The sulfate process is older and is the process employed by most of the existing worldwide

TABLE 20

#### $TiO_2$ CAPTIVE CONSUMPTION (Thousands of Tons)

Year	Total Shipments	Commercial Shipments	Captive Consumption <sup>1</sup>	Percent Apparent Consumption
1965	573.0	524.5	48.5	8.0
1966	593.3	545.5	47.8	7.6
1967	582.3	547.5	39.8	6.4
1968	632.1	564.4	67.7	10.1
1969	654.5	590.1	64.4	9.4
1970	643.7	560.9	82.8	12.0
1971	684.7	581.2	103.5	14.3

<sup>1</sup>Captive consumption is calculated as total shipments - commercial shipments.

Source: Current Industrial Reports, U.S. Department of Commerce.

capacity. The chloride process was developed in the 1950's and is used in all new  $\text{TiO}_2$  plants built in the U.S. since 1956. In recent years chloride process plants have become increasingly widespread in Europe as well.

#### (1) Sulfate Process

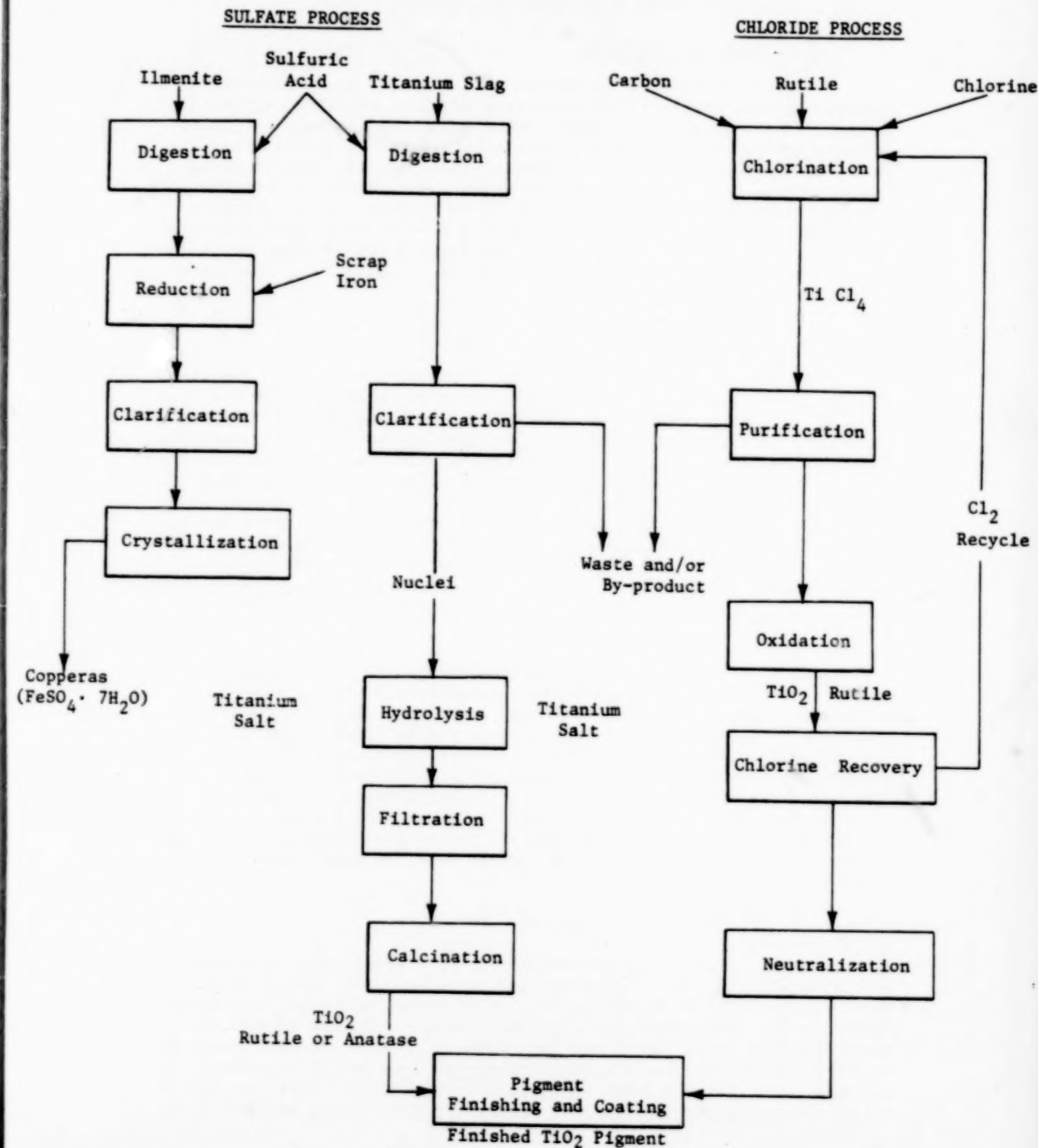
Figure 7 left-hand side, is a schematic representation of the sulfate process. In the first step ilmenite, an ore or sand containing 40-60%  $\text{TiO}_2$ , or titanium slag, containing 60-70%  $\text{TiO}_2$ , is digested with sulfuric acid. The amount of acid required ranges from 2.5 to 4.5 pounds per pound of finished pigment and depends on the  $\text{TiO}_2$  content of the ore. In addition to the formation of titanium sulfate salts, substantial amounts of ferrous sulfate are also formed since the other major component of ilmenite is iron oxide,  $\text{FeO}$ . The remainder of the process involves separating the various sulfate salts, with iron being removed from the process as hydrated ferrous sulfate, copperas, and  $\text{TiO}_2$  being precipitated in the hydrolysis step. This final chemical form of the  $\text{TiO}_2$  pigment, anatase or rutile, is determined by the nucleus crystal used to seed precipitation in this step. The  $\text{TiO}_2$  precipitate is next calcined at temperatures of up to  $1250^\circ\text{C}$ , during which adsorbed sulfur trioxide and water are driven off and, if rutile seeds were used in the hydrolysis step, rutile-type pigment is formed. The pigment finishing process will be described later.

#### (2) Chloride Process

The chloride process typically utilizes rutile ore containing 90% to 97%  $\text{TiO}_2$  as its raw material. Du Pont has developed the capability to use ilmenite, thereby lowering its raw material costs significantly. Figure 7 right-hand side, outlines the process. In the first step, rutile ore is burned with chlorine gas to produce titanium tetrachloride. This material is separated from the reaction mixture via distillation, then is oxidized at high temperature to produce  $\text{TiO}_2$  particles, which are quickly quenched. The quenching process allows extremely close control of pigment particle size which is essential in developing hiding power of the pigment. Chlorine is recovered in the oxidation process and is recycled for use in the first step. As in the sulfate process, the refined  $\text{TiO}_2$  pigment is sent to finishing steps which enhance the surface properties of the pigment particles.

Although the chloride process is conceptually straightforward and does not produce the substantial quantities of waste materials that the sulfate process does, it has been extremely difficult to operate commercially. One problem has been the extreme corrosiveness of the high temperature chlorine employed. A second, more fundamental problem, has been the oxidation step, which is extremely sensitive to burner configuration and to product recovery methods. Du Pont is the most successful in this regard and holds significant patent protection in this technology.

FIGURE 7  
 $\text{TiO}_2$  PIGMENT MANUFACTURING PROCESSES





### (3) Pigment Finishing

Before pigment from either process is sold, it is processed through a series of finishing operations in which specific particle surface properties are developed. These properties in turn determine characteristics such as pigment dispersibility and durability. For instance, pigment intended for plastics use is usually treated with an organic agent, dimethyl siloxane, to enhance the pigment's compatibility with the plastic system. Sulfate producers have made their pigments more competitive with chloride pigments in recent years through careful control of particle size and coating characteristics obtained in finishing operations. Such finishing steps generally add 1-2¢ to the basic manufacturing cost of the pigment.

#### b. Producers

At the end of 1972, there were 11 domestic  $TiO_2$  producers operating 15 plants, all but one of which are in the eastern half of the U.S. Table 21 summarizes pertinent information regarding these facilities. Since 1956, chloride process facilities have accounted for all new  $TiO_2$  pigment plant construction. Possibly reflecting producer's uncertainty about process technology and economics, individual capacity of most chloride plants is in the 25,000 to 30,000 ton range. The notable exception is Du Pont, which is increasing the capacity of their New Johnsonville, Tennessee, plant to 195,000 tons by year-end 1973 and is actively considering a new 100,000 ton chloride facility in Georgia. Two producers, PPG and NL Industries, have recently closed their chloride facilities, moves reportedly due to raw material supply and economics problems.

Several of the large producers--Du Pont, NL Industries, and Glidden-Durkee--have integrated their operations backward to provide captive supplies of ilmenite ore. (No domestic producer has a captive source of rutile as virtually all of this raw material is imported from Australian producers.) These three producers have also achieved forward integration through captive  $TiO_2$  supply for their paint products. No other domestic producers have achieved integration to a comparable extent. Most  $TiO_2$  plants are isolated manufacturing facilities, although a few are part of larger, multi-product facilities, and most plants produce and sell titanate and other salts as by-products from the process.

#### c. Manufacturing Economics

Tables 22 and 23 summarize estimated manufacturing economics and profitability for a 25,000 ton sulfate plant. The costs for raw materials, utilities, direct labor, and overhead, are based on current estimates for these items. For the sulfate process, two investment bases are used--replacement and depreciable. The replacement basis is an ADL estimate of current plant replacement cost and is used for calculation of insurance and maintenance, since these items are best reflected by current costs and replacement value. A depreciable basis

TABLE 21  
 $TiO_2$  MANUFACTURING LOCATIONS AND CAPACITIES  
(Thousands of Tons)

Company	Location	Annual Capacity	Process <sup>4</sup>	Raw Material	Start-Up Year
American Cyanamid	Savannah, Ga.	70 40 110	S C	Imported ilmenite, slag Imported rutile	1955 1966
Cabot	Ashtabula, Ohio <sup>5</sup>	27	C	Imported rutile	1964
Combustion Engineering	Camden, N.J. Wilmington, Del.	n.a. n.a.			
E.I. Du Pont	Antioch, Cal. Edgemoor, Del. <sup>1</sup>	27 100	C S C	Imported rutile Captive ilmenite, slag Captive mixture of ilmenite/ leucosene, imported rutile/ Captive mixture of ilmenite/ leucosene, imported rutile	1963 1935 1956 1959
N.J. Zinc (Div. of G&W)	New Johnsonville, Tenn. <sup>2</sup>	141	C		
Kerr-McGee	Gloucester City, N.J.	268	S	Slag	1946
Lonza	Hamilton, Miss. Mapleton, Ill.	45 n.a.	C	Imported rutile	1965
N.L. Industries	St. Louis, Mo. Sayreville, N.J. <sup>3</sup>	108 115 223	S S C	Captive ilmenite Captive ilmenite Imported rutile	1923 1918 1966
Glidden-Durkee (Div. of SCM)	Baltimore, Md.	50 25 75	S C	Captive ilmenite, slag Imported rutile	1956 1970
Sherwin-Williams	Ashtabula, Ohio	27	C	Imported rutile	1969
Transelco	Penn Yan, N.Y.	n.a. 817			

<sup>1</sup>Converting to all-chloride process and expanding to 112,000 tons by year end 1973.  
<sup>2</sup>Expanding to 195,000 tons by year end 1973.  
<sup>3</sup>Announced closing January 1973.  
<sup>4</sup>S = Sulfate; C = Chloride.  
<sup>5</sup>Plant being operated by N.J. Zinc (Div. of G&W) under lease-purchase agreement.



TABLE 22

TiO<sub>2</sub> MANUFACTURING ECONOMICS--SULFATE PROCESS

Basis: Sulfate Process  
 25,000 T/Yr, 100% of Capacity  
 330 Days/Yr  
 Replacement Investment--\$26,325,000<sup>1,3</sup>  
 Depreciable Investment--\$15,000,000

Item	Unit	\$/Unit	Units/Ton	\$/Ton Pigment
<u>Raw Materials</u>				
Ilmenite (56% TiO <sub>2</sub> )	Ton	21.00	1.87	39.27
Sulfur	Ton	30.00	0.88	26.40
Caustic	Ton	55.00	0.20	11.00
Other Chemicals	---	---	---	30.00
				106.27
<u>Utilities</u> <sup>2</sup>				
Water	MGal	0.10	220	22.00
Electricity	kwh	0.014	525	7.35
Natural Gas	MMBtu	0.60	10	6.00
				35.35
<u>Direct Labor</u> <sup>2,4</sup>				
Supervision	Man Hr	7.50	1.58	11.85
Operators	Man Hr	5.00	4.43	22.15
Helpers	Man Hr	4.00	3.80	15.20
				49.20
<u>Overhead</u>				
@ 100% Direct Labor	---	---	---	49.20
<u>Maintenance, Labor, and Supplies</u>				
@ 7% of Replacement Investment/Yr				73.71
<u>Depreciation</u>				
@ 9.1% of Depreciable Investment/Yr				54.60
<u>Insurance and Local Taxes</u>				
@ 2.0% of Replacement Investment/Yr				21.06
Total Manufacturing Cost Per Ton				\$389.39
Manufacturing Cost Per Lb. Pigment				\$ 0.195

<sup>1</sup>Capital investment based on Contractor's estimates.

<sup>2</sup>Assumes wage rates and utilities rates of New Jersey area.

<sup>3</sup>Assumes capital cost of H<sub>2</sub>SO<sub>4</sub> plant included. Does not include solid waste handling capital or operating costs.

<sup>4</sup>See labor schedule included.

Source: Contractor's estimates.

TABLE 22 (Continued)

LABOR SCHEDULE  
TiO<sub>2</sub> PRODUCTION--SULFATE PROCESS

	Supervisors	Operators	Helpers
Feed Preparation Section	1	1	2
Digestion and Separation Section		4	3
Hydrolysis--Precipitation Section	1	3	2
Purification Section	1	1	1
Calcination--Dry Milling Section	1	1	1
After Treatment Section	1	3	3
Sulfuric Acid Plant	---	1	---
Total--Men/Shift	5	14	12

TABLE 23

TiO<sub>2</sub> PIGMENT PROFITABILITY--SULFATE PROCESS

Investment: \$15,000,000  
 Manufacturing Cost: \$0.195

	(Rutile Grade)	(70/30 Rutile/Anatase Mix)	(Anatase Paper Grade)
Pigment Selling Price	\$0.275/Lb.	\$0.26/Lb.	\$0.24/Lb.
Gross Profit/Lb.	0.080	0.065	0.045
Gross Profit/Ton	160.00	130.00	90.00
Freight at 5% of List Price Sales/Ton	27.50	27.50	27.50
General, Selling, & Administrative @ 7.5% of List Price Sales/Ton	41.25	41.25	41.25
Profit Before Taxes/Ton	91.25	61.25	21.25
Profit After Taxes/Ton	46.62	30.62	10.62
Profit After Taxes as % of Sales	8.3	5.9	2.2
	<u>CASH FLOW</u>		
Profit After Taxes/Ton	46.62	30.62	10.62
Plus Depreciation/Ton	54.60	54.60	54.60
Total Cash Flow/Ton	101.22	85.22	65.22
Total Cash Flow @ 25,000 Tons	2,540,000	2,130,000	1,630,000
Investment	15,000,000		
Working Capital (3 months' operating costs)	2,433,000		
	17,433,687		
Payback (Yrs)	6.9	8.2	10.7
% Return on Capital Employed	15.0	12.0	9.3

Source: Contractor's estimates.

of smaller dollar size than replacement value is used for depreciation since most sulfate plants are 20 to 30 years old, and current depreciable assets are restricted to recently replaced process equipment and newly installed finishing equipment. A depreciation rate of 9.1% per year is used as this rate is the highest allowed by the Internal Revenue Service for chemical industry facilities. Since all TiO<sub>2</sub> grades are sold on a delivered basis, a freight charge of 5% of list price has been included in Table 23. General selling and administrative charges of 7.5% of list price sales reflect the relatively expensive selling effort required for TiO<sub>2</sub> pigments.

Table 23 shows that depending on grade and price, after tax profitability ranges from 7.1% down to 2.2% of sales. In addition, return on capital could theoretically be as high as 13.7% after tax, although 11.5%, based on a product mix of 70:30 rutile/anatase grades, is probably more representative of actual industry performances.

Tables 23 and 24 detail similar costs and profitability figures for a 25,000-ton chlorine plant. The depreciable and replacement investment basis are considered the same in this case since most chloride plants not only are relatively new with substantial original book value remaining, but also have experienced the updating of process and finishing equipment found in sulfate process plants. As seen in Table 25, while the after-tax profit percentage is low, 3.6%, the return on capital, at 10.2%, is considerably higher. By virtue of a large depreciation tax shield, the chloride process apparently generates substantial cash flow, despite low-book profits. It should be noted that chloride profit margins have shrunk recently, largely due to the dramatic rise in rutile ore prices, now \$175 per ton and higher. Ore cost comprises over 50% of the cost of manufacture, and this item has been most responsible for the elimination of the chloride process' earlier cost advantage over the sulfate process. Chloride pigment producers are anxious to see this cost drop through either more widespread use of ilmenite or through successful commercialization of synthetic rutile production. An important factor in economical chloride production is recovery and recycle of chlorine gas after the oxidation step. The highly corrosive nature of chlorine makes this step difficult, but failure to do so can result in extraordinarily high use of make-up chlorine.

#### d. Raw Materials

Ready availability of inexpensive raw materials is one of the key requirements for the continued production of low-cost TiO<sub>2</sub> pigments. Economic production via the chloride process has been seriously threatened by the recent, dramatic increase in rutile ore prices. In contrast, ilmenite prices have risen only slightly to \$35 per ton. The reason for these different behaviors is the supply/demand balance for each ore.

Ilmenite is mined virtually worldwide, with 1971 world production being almost 2.9 million short tons. U.S. ilmenite production has declined from 930,000 tons in 1969 to 680,000 tons in 1971, but worldwide

TABLE 24

TiO<sub>2</sub> MANUFACTURING ECONOMICS--CHLORIDE PROCESS

Basis: Chloride Process  
 25,000 T/Yr, 100% of Capacity  
 330 Days/Yr  
 Investment (Depreciable and  
 Replacement)--\$21,330,000<sup>1</sup>

Item	Unit	\$/Unit	Units/Ton	\$/Ton Pigment
<u>Raw Materials</u>				
Rutile	Ton	175.00	1.17	204.75
Coke	Ton	24.00	0.35	8.40
Chlorine	Ton	50.00	0.21	10.50
Chemical Additives	---	-----	----	7.00
				230.65
<u>Utilities</u> <sup>2</sup>				
Water	MGal	0.10	23	2.30
Electricity	kwh	0.014	750	10.50
Natural Gas	MMBtu	0.60	10	6.00
Refrigeration	Ton/Day	3.00	2.5	7.50
				26.30
<u>Direct Labor</u> <sup>3</sup>				
Supervision	Man Hr	7.50	0.95	7.12
Operators	Man Hr	5.00	5.4	27.00
				34.12
<u>Overhead</u>				
@ 100% Direct Labor				34.12
<u>Maintenance, Labor, and Supplies</u>				
@ 6% of Investment/Yr				51.19
<u>Depreciation</u>				
@ 9.1% of Investment/Yr				77.63
<u>Insurance and Local Taxes</u>				
@ 2% of Replacement Investment/Yr				17.06
Total Manufacturing Cost Per Ton				\$454.01
Manufacturing Cost/Lb Pigment				\$ 0.227

<sup>1</sup>Capital Investment based on Contractor's estimates.  
<sup>2</sup>Assumes wage and utilities rates of New Jersey.  
<sup>3</sup>See labor schedule included.

TABLE 24 (Continued)

LABOR SCHEDULE  
TiO<sub>2</sub> PRODUCTION--CHLORIDE PROCESS

<u>Operators</u>	<u>Men/Shift</u>
Load in	1
Chlorination reactor	1
Quench, TiCl <sub>4</sub> recycle, storage	1
Sludge filter, waste	1
TiCl <sub>4</sub> purification	2
TiCl <sub>4</sub> vaporizer, preheat, additives	1
Oxidation chamber	1
TiCl <sub>4</sub> quench, cyclones, bag filter	1
Chlorine recovery	1
After treatment	4
Bagging, warehouse	2
Oxygen plant	1
	1
Total	17
<u>Supervisors</u>	
Chlorination, purification	1
Oxidation	1
After treatment	1
	1
Total	3



TABLE 25

TiO<sub>2</sub> PIGMENT PROFITABILITY--CHLORIDE PROCESS

Investment: \$21,330,000  
 Manufacturing Cost: \$0.227/Lb.

<u>Pigment Selling Price</u>	(Rutile Grade) <u>\$0.275/Lb.</u>
Gross Profit/Lb.	0.048
Gross Profit/Ton	96.00
Freight at 5% of List Price Sales/Ton	27.50
General, Selling, & Administrative @ 7.5% of List Price Sales/Ton	<u>41.25</u>
Profit Before Taxes/Ton	27.25
Profit After Taxes/Ton	13.625
Profit After Taxes as % of Sales	2.5
<u>CASH FLOW</u>	
Profit After Taxes/Ton	13.62
Plus Depreciation/Ton	<u>77.63</u>
Total Cash Flow/Ton	91.25
Total Cash Flow @ 25,000 Tons	2,281,375
Investment	21,330,000
Working Capital (3 months' operating costs)	<u>2,837,500</u>
	24,167,500
Payback (Yrs)	10.6
% Return on Capital Employed	11.7

supply has been filled by increased production in Australia and Norway. Present reserves of ilmenite are such that, at the present annual world consumption rate of nearly three million tons, adequate supplies of sufficient quality ore should be available for nearly 100 years.

The rutile ore supply situation, however, is not so bright. Rutile production in recent years has remained constant at slightly over 400,000 tons and is confined almost exclusively to the east coast of Australia. Significant deposits are believed available in Sierra Leone, but technical problems have hampered attempts to exploit this source. There is no rutile ore mined in the U.S. A large increase in worldwide chloride pigment process capacity has greatly increased demand, and present rutile reserves are estimated to be barely 20 years. These conditions have fostered a rise in rutile ore price from \$100 per ton in 1965 to \$180 per ton presently.

A major hope in the bleak rutile supply situation is the commercialization of synthetic rutile production. This process involves chemical leaching of ilmenite ore to remove iron impurities and to upgrade the TiO<sub>2</sub> content to approximately 90%. Since nearly two tons of ilmenite are required to produce one ton of synthetic rutile, waste disposal considerations will adversely affect the rapid development of domestically available synthetic rutile, although both Sherwin-Williams and Kerr McGee are actively pursuing this technology. Semi-commercial synthetic plants are in operation in Australia and Japan, and the product has been tested and found acceptable in most U.S. chloride process pigment plants. Chloride producers anticipate that synthetic rutile will begin to appear commercially by 1975 at \$130-150 per ton and feel that this material will be significant in keeping chloride pigment production economically viable.

The other significant factor in chloride process raw materials has been the development of Du Pont's ability to utilize ilmenite ore in its chloride plants. Although this capability has always been technically feasible, it has been uneconomic due to the high chlorine loss resulting from chlorinating the 40% of iron oxide present in ilmenite. Du Pont, however, has developed the ability to minimize chlorine use and is able to produce chloride pigment for an estimated 1-2¢ per pound less than rutile-based chloride processes. Since ilmenite is much more widely available than rutile, other chloride producers are working on both ilmenite beneficiation technology and direct ilmenite use capability in chloride processing. Thus far, however, Du Pont remains the only producer using ilmenite directly.

The last major source of TiO<sub>2</sub> is titanium slag, which is produced in Canada from plentiful, low-quality ilmenite ores. The ilmenite used here is closely intermixed with iron ores, and smelting is employed to produce pig iron and titanium slag containing 70% to 72% TiO<sub>2</sub>. Slag cannot be used in the chloride process due to the formation of insoluble chloride salts which plug up processing equipment. While other raw materials such as chlorine, coke, and sulfuric acid are used in

TiO<sub>2</sub> pigment production, these items are widely available and do not constrain the production process to the degree that TiO<sub>2</sub> ores do.

#### 4. Supply/Demand Balance; Prices

Industry capacity has been sufficient to supply demand as almost continual additions to capacity have been made. Table 26 summarizes capacity and production figures for recent years and shows that capacity utilization has been in the 75% to 85% range. Capacity has been taken at announced, or nameplate, levels and is higher than effective capacity due to grade/product mix constraints. The industry is now facing a tight-supply situation with NL Industries announcing the closing of its chloride facilities in Sayreville, New Jersey. Du Pont's announced expansions won't be operational until year-end 1973.

This supply situation is substantially different from that of 1970-71 when over-supply forced a sharp depression in prices. Table 27 summarizes recent shipment valuation history and confirms industry claims that the 1970-71 period saw severe price competition, despite stable list prices. Demand and prices have improved with the economic recovery and recent list prices stand at: standard anatase and rutile grades, bulk--28.5¢ per pound; paper grade anatase--24¢ per pound. Most producers are running at full capacity presently, and shipments are being made at list prices.

TABLE 26

#### TiO<sub>2</sub> INDUSTRY PLANT CAPACITY UTILIZATION (Thousands of Tons)

	<u>Capacity</u>	<u>Production</u>	<u>Percent Utilization</u>
1965	713	576.7	81
1966	725	594.5	82
1967	766	589.4	77
1968	746	623.7	84
1969	778	664.3	85
1970	817	655.3	81
1971	805	677.8	84
1972	817	687.3	84

Sources: Chemical Economics Handbook and Current Industrial Reports.

TABLE 27

TiO<sub>2</sub> COMMERCIAL SHIPMENT VALUES  
(Shipments in Thousands of Tons)

	Commercial Shipments	Total Value <sup>1</sup>	Value/Lb. <sup>2</sup>	List Prices <sup>3</sup>	
				Anatase	Rutile
1965	524.5	274.7	.261	.25	.26
1966	545.4	279.7	.256	.25	.26
1967	542.6	277.2	.255	.25	.26
1968	564.4	288.8	.256	.25	.26
1969	590.1	301.1	.255	.26	.27
1970	560.9	277.8	.248	.26	.27
1971	581.2	262.4	.226	.26	.26

<sup>1</sup>Value in \$ Millions.  
<sup>2</sup>Value in \$ per Pound.  
<sup>3</sup>Carlot, \$ per Pound.

Source: Current Industrial Reports, U.S. Department of Commerce.

D. SODIUM CHROMATE AND BICHROMATE

1. Summary

The U.S. sodium bichromate market has been characterized by essentially static demand during the past five years at approximately 150,000 tons annually. The market outlook for the next five years is for a slight overall contraction in demand with deteriorating markets in water treating and textiles (resulting from more stringent water quality standards) only partially offset by modest demand growth for chromic acid, chrome colors and catalyst applications. Very nearly half of current demand for sodium bichromate is for chrome colors and chromic acid. Other uses include leather tanning, metal treating, textiles, water treating and catalyst manufacture. Substitute products (or processes) exist for most bichromate derivatives, constraining demand growth.

There are currently three producers of sodium chromate and bichromate--Allied Chemical, Diamond Shamrock and PPG Industries. Aggregate captive requirements of these three companies approximate 35% of current production. U.S. producers of sodium bichromate are dependent on foreign sources, primarily the Republic of South Africa, for chromite ore, the basic raw material.

Manufacturing costs are estimated at \$212 per ton. Assuming GS&A at 5.5% of sales and a weighted average selling price of \$262 per ton (including some chrome salt cake by-product credit), the industry after-tax income in 1972 approximated \$18.50 per ton, equivalent to a 7.1% return on sales.

During the period 1960-1971, actual prices (as calculated from Commerce Department data for dollar values and tonnages) received by the industry have remained in a remarkably narrow range between \$240 and \$255 per ton. Although confirming Commerce Department data are not yet available, list price increases made recently probably have been reflected in somewhat higher plant prices. These price increases are believed to have been made possible primarily as a result of a somewhat less aggressive posture by foreign production sources, notably Italy and Japan. Producers in both these countries are understood to be facing higher manufacturing costs as a result of more stringent water pollution abatement standards. Nonetheless, imports have exceeded exports in seven of the last ten years.



## 2. Market Characterization

In Table 28 is shown the apparent U.S. consumption of sodium chromate and bichromate for the period 1960 through 1972. For most of this period, U.S. production, as reported by the Department of Commerce, has varied between 135 and 155 thousand tons annually. As indicated, these data include both sodium chromate and sodium bichromate. While some of the sodium chromate produced in the initial phase of the manufacturing process is marketed as such (an estimated 15 thousand tons of bichromate equivalent), most of the sodium chromate filtrate is further processed to produce sodium bichromate.

Imports, primarily from the U.S.S.R. and Japan in 1972, have varied in the last several years between 3.5 and 6.5 thousand tons. The sharp drop in imports from 1966 to 1967 reflected decreased U.S. demand. As a result of the Kennedy round agreements, the import rate of duty was reduced to \$0.87 per pound as of January 1, 1972.

Exports, primarily to Canada, have trailed imports in recent years. In 1972 exports totaled 4.03 thousand tons valued at \$0.93 million. Canada received the bulk (70%) of 1972 exports, with Colombia next at very nearly 20%. For purposes of estimating apparent consumption, we have ignored changes in stocks of chromium chemicals at producer plants.

On a long-term basis (in the post-World War II period), apparent U.S. consumption of sodium chromate and sodium bichromate has increased at an average annual compound rate of 2.4% per year. In each of the last three years, however, consumption has declined; the outlook is for a continuation of the recent trend.

### a. Uses

In Table 29 is shown the estimated 1971 use pattern for sodium chromate and bichromate. Very nearly 50% is consumed in the manufacture of chrome colors and chromic acid. In descending order of bichromate consumption, the most important chromate colors are chrome yellow and orange, chromium oxide green, molybdate orange, and zinc yellow and chrome green. Production of chromium pigments in 1971 and the estimated bichromate equivalent requirements is shown in Table 30. Requirements for U.S. sodium bichromate in pigment production would have been higher were it not for the substantial imports of chrome colors. Imports of chromium-containing pigments in 1971 included chromium yellow, 6.2 thousand tons; chromium oxide green, 0.9 thousand tons; chrome green, 0.3 thousand tons; zinc yellow 1.08 thousand tons; and molybdate orange, 0.3 thousand tons. Total value of these products and miscellaneous other chrome colors was \$4.5 million, 17% higher than in 1970.

A major use for chrome yellow is the yellow center strip line for highways. Chromium oxide green is used where chemical and heat resistance is required, e.g., in ceramic colors, for coloring cement and in green asphalt roofing. Zinc yellow finds application as a corrosion inhibitor

TABLE 28

### APPARENT U.S. CONSUMPTION OF SODIUM CHROMATE AND BICHROMATE (Thousands of Short Tons, $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ )

Year	Production	Imports	Exports	Apparent Consumption
1960	121.9	1.9	9.6	114.2
1961	120.9	1.6	7.1	115.4
1962	127.5	2.5	5.0	125.0
1963	133.9	3.5	5.1	132.3
1964	137.9	3.4	6.7	134.6
1965	141.0	18.0	4.0	155.0
1966	141.5	24.1	2.6	163.0
1967	135.3	8.2	3.3	140.2
1968	146.0	11.6	4.8	152.8
1969	152.6	6.5	5.1	154.0
1970	153.5	3.6	4.9	152.2
1971	138.2	6.4	3.1	141.5
1972	137.1	5.7	4.0	138.8

Source: U.S. Department of Commerce.

TABLE 29

ESTIMATED 1971 USE PATTERN FOR SODIUM CHROMATE AND BICHROMATE  
(Thousands of Tons)

<u>End-Use</u>	<u>Consumption</u>
Pigments	36.2
Chromic acid	32.0
Leather tanning	28.0
Metal treating	16.2
Textiles and dyes	10.1
Miscellaneous	19.0
Total	141.5

Source: Contractor's estimates.

TABLE 30

PRODUCTION OF CHROMIUM PIGMENTS AND CONSUMPTION OF SODIUM BICHROMATE EQUIVALENT, 1971  
(Thousands of Tons)

<u>Pigment</u>	<u>Production</u>	<u>Consumption of Bichromate Equivalent</u>
Yellow and Orange	29.0	14.8
Oxide Green	6.6	9.0
Molybdate Orange	11.4	5.9
Zinc Yellow	5.6	5.8
Chrome Green	2.7	0.7
	55.3	36.2

Source: U.S. Department of Commerce and Contractor's estimates.

for light metals and steel. For example, in combination with red lead it is used in priming structural steel. It also is part of the formulation for automotive body prime coats. Sodium bichromate-based pigments are also used in printing inks and plastics.

The second largest outlet for sodium bichromate is for the manufacture of chromic acid, produced by reacting concentrated sulfuric acid with sodium bichromate. Chromic acid, in turn, is used primarily in chrome plating processes but also finds use in copper stripping, aluminum anodizing and for general corrosion prevention. The automotive industry represents the major user for chrome plating, although other durable goods manufacturing such as appliances also have requirements. Chromic acid imports have constrained domestic production.

The third most important outlet for sodium bichromate is leather tanning. With the exception of heavy cattle hides, where vegetable tanning is used, chrome tanning is the most important treatment for all hides (i.e., calfskins, goat- and kidskins, sheep- and lambskins). Chrome tannage is used in shoe uppers, glove leathers, garment leathers, and bag leather. In the tanning process, sodium bichromate is reduced with glucose to make the solutions of chromium salts employed in chrome leather tanning.

Various metal treating and finishing processes are the next most important outlet for sodium bichromate. For example, a solution of sodium bichromate and sulfuric acid is used in the bright dipping of brass and copper to remove oxide scale. Another important use in metal finishing is in the formation of chemical conversion coatings to provide corrosion protection and decorative effects, as well as to provide a good base for painting metal surfaces.

In the textile industry, sodium bichromate is used in a variety of ways. For example, among its applications are mordanting of wool, dyeing nylon and wool, dyeing with chromate colors, as an after-treatment on cotton to retard fading of dyes during washing and for striped wool.

A miscellaneous category of uses, including chemical applications, wood preservative applications and corrosion control, accounted for approximately 13% of U.S. sodium bichromate consumption in 1971. A small quantity of sodium bichromate is used in the oxidation of various organic chemicals, including pharmaceuticals. The bleaching of fats, oils, and waxes also requires use of the bichromate as an oxidant. Perhaps the major chemical use for sodium bichromate is in the manufacture of catalysts. Chromates and bichromates are an important ingredient in the preservatives and fire retardants used by the wood preserving industry. Chromates are also used to inhibit corrosion in recirculating water-based systems (e.g., in cooling towers and large central air conditioning facilities).

### b. Substitute Products

The primary substitution effect is represented by alternate materials (or processes) for derivatives of sodium bichromate rather than for the bichromate per se. As an example, aluminum or high-impact plastics can be substituted for chrome plated trim on motor vehicles. (It should be noted that processes have been developed to chrome plate plastics, e.g., ABS, although uncoated plastics are also used in automobile trim.) As another example, cadmium yellow can be used in place of chrome yellow pigments. Market growth for chrome leather is limited by lower cost substitutes, specifically, the poromeric materials. Tin-free steel cans coated with chrome compete with aluminum cans and seamless, deep-drawn steel cans coated with tin. The existence of these alternate materials both limits market growth and represents a constraint on higher sodium bichromate prices.

### c. Captive Requirements

Table 31 presents Commerce Department data for sodium chromate and bichromate production, shipments, and shipment value for the period 1960 to 1971. Excluding inventory fluctuations and losses, the difference between total production in any given year and the quantity of shipments reflects the amount of sodium bichromate consumed at the producing plants for derivative manufacture. In recent years, this has amounted to about 50,000 tons or approximately 33% of total production. Including inter-plant transfers, captive consumption by the industry approximates 35% of production.

## 3. Supply Characterization

### a. Manufacturing Routes and Economics

Sodium chromate and bichromate are made by calcining chrome ore (chromite) with soda ash or with soda ash and lime. More specifically, sodium chromate is manufactured by calcining a mixture of chromite ore, lime, and soda ash. The sodium chromate, if desired, can be recovered by leaching and crystallization. Sodium bichromate is produced by treating a sodium chromate solution with sulfuric acid. Sodium bichromate and the sodium sulfate by-product produced are separated and recovered by crystallization. Sodium bichromate is the principal commercial product because it is usually priced to cost less per unit of  $\text{CrO}_3$  than sodium chromate.

As indicated, chromium chemicals are produced from chromite ore, the term chromite being a general one used to designate chromium-bearing spinel. The composition of chromite varies widely, usually with inclusions of magnesia, alumina, and silica. Although distinctions are not clearcut, there are three broad grades of chromite--high chromium chromite, a metallurgical grade; high-iron chromite, which is the chemical grade; and high-aluminum chromite, the refractory grade. Chromite



TABLE 31

## SHIPMENTS OF SODIUM CHROMATE AND BICHROMATE

Year	Production (M Tons)	Shipments*		Unit Value (\$/Ton)
		Quantity (M Tons)	Value (\$ MM)	
1960	121.9	89.1	22.7	254.77
1961	120.9	85.2	20.5	240.61
1962	127.5	97.0	24.8	255.67
1963	133.9	88.2	21.2	240.36
1964	137.9	99.6	22.9	239.92
1965	141.0	103.7	24.2	233.37
1966	141.5	94.2	23.9	253.72
1967	135.3	94.0	23.0	244.68
1968	146.1	100.0	23.9	239.00
1969	152.6	97.5	23.1	236.92
1970	153.5	103.2	24.8	240.31
1971	138.2	88.2	21.9	248.30

\*Including interplant transfers.

Source: U.S. Department of Commerce.

has not been mined in the U.S. since 1961, when a small tonnage was produced under the government's Defense Production Act. With the exception of government stockpile releases, U.S. producers of chromium chemicals are therefore dependent on foreign sources. No commercially feasible process for upgrading domestic chromite bearing materials to compete with foreign ores has been developed.

Most of the known world reserves are located in the Republic of South Africa and Southern Rhodesia. The embargo on chromite from Southern Rhodesia, brought about by United Nations action in 1966 and an Executive Order in 1967, resulted in the U.S. turning to the U.S.S.R. for some of its chromite requirements. Most of the chemical grade chromite, however, comes from the Republic of South Africa.

Estimated manufacturing costs for sodium bichromate are shown in Table 32. The manufacturing cost estimates are based on a plant with 150 tons per day capacity and an investment (assuming the plant was built in 1960) of \$5.7 million. The indicated manufacturing cost is \$212. Included in this total is the cost of producing by-product sodium sulfate, amounting to approximately \$20 per ton of bichromate.

Assuming a 1972 selling price for sodium bichromate of \$245 per ton, plus by-product credit for 0.8 tons of sodium sulfate valued at \$17, the total unit sales value is \$262. Taking GS&A at 5.5% of sales, the indicated after-tax profit is \$18.50 per ton for an after-tax return on sales of 7.1%.

#### b. Supply/Demand Balance

The producers of sodium bichromate are shown on Table 33. The two largest producers, Allied Chemical and Diamond Shamrock, have heavily integrated positions, both with respect to raw materials and derivative products. For example, Allied is a major producer of soda ash and sulfuric acid, and, along with Diamond Shamrock, is a major producer of chromic acid. Similarly, Diamond Shamrock produces both soda ash and sulfuric acid and several other derivatives of sodium bichromate in addition to chromic acid. PPG Industries produces soda ash at Corpus Christi and has nominal captive outlets for the sodium bichromate in pigments. Hercules, Inc., had produced bichromate in a small (approximately 30 tons per day) plant in Glens Falls, N.Y., for captive consumption in pigment manufacture. This facility has been closed.

The newest facility of the three producing plants is Diamond Shamrock's. Diamond Shamrock brought its Castle Hayne, North Carolina, facility on-stream late in 1971. The new plant replaced two older, less efficient plants at Painesville, Ohio, and Kearny, New Jersey. Including Diamond's new facility, total industry capacity is estimated at 175,000 tons per year. Compared with reported production of 137-138,000 tons per year, the industry operating rate in both 1971 and 1972 was slightly under 80%.

TABLE 32

## ESTIMATED MANUFACTURING COST, SODIUM BICHROMATE

Production: 150 Tons/Day sodium bichromate  
 Operation: 330 operating days  
 Investment: \$5,700,000 (Assuming plant was built in 1960)

Item	Units	US\$/Unit	Units/Ton	Cost (US\$/Ton Product)
Raw Materials				
Chromite (44% Cr <sub>2</sub> O <sub>3</sub> )	short ton	19.00	1.30	24.60
Soda Ash (Na <sub>2</sub> CO <sub>3</sub> )	100 lb	2.40	17.00	40.80
Lime (CaO)	short ton	20.50	0.80	16.40
Sulfuric Acid (66°Be)	short ton	26.00	0.50	13.00
Utilities				
Power	MKwh	15.00	0.50	7.50
Fuel	MMBtu	0.70	40.00	28.00
Water	MGal	0.10	14.00	1.40
Direct Labor				
Supervisors	Man-hr	7.50	0.17	1.30
Operators	Man-hr	5.00	3.40	17.00
Helpers	Man-hr	3.75	6.00	22.50
Overhead	60% Direct Labor			24.48
Maintenance				5.50
Maintenance Supplies				4.00
Depreciation	(3.0% of investment)			3.52
Taxes and Insurance	(1.3% of investment)			1.50
Total Manufacturing Cost				211.50

Source: Contractor's estimates.

TABLE 32 (Continued)

MANUFACTURING COSTS FOR BY-PRODUCT Na<sub>2</sub>SO<sub>4</sub>

	Units	US\$/Unit	Units/Ton	US\$/Ton
Utilities				
Power	MKwh	15.00	0.10	1.50
Water	MGal	0.10	30.00	3.00
Direct Labor				
Supervisor	Man-hr	7.50	0.30	2.20
	Man-hr	5.00	1.00	5.00
	Man-hr	3.75	2.00	7.50
Maintenance Supplies	(0.4% of total investment)			0.50
Maintenance Labor	(0.2% of total investment)			0.20
Tax and Insurance	(0.1% of total investment)			0.10
				20.00

Source: Contractor's estimates.

TABLE 33  
  
CURRENT PRODUCERS OF SODIUM BICHROMATE  
(Thousands of Tons Hydrous Sodium Bichromate Equivalent)

<u>Company</u>	<u>Location</u>	<u>Capacity</u>
Allied Chemical Corp.	Baltimore, Md.	75
Diamond Shamrock Corp.	Castle Hayne, N.C.	70
PPG Industries, Inc.	Corpus Christi, Tex.	<u>30</u>
Total		175

Source: Trade sources.

#### 4. Prices

A comparison of list prices versus actual prices as calculated from the Commerce Department data on reported value and quantity of shipments is shown in Table 34. Throughout the period, actual unit values realized by producers have been less than list prices. For example, in 1971 the actual price was 12.4 cents per pound versus a list price of 16.0 cents per pound.

List prices were increased by approximately 1 cent per pound in 1973 as they were in 1970 and 1971. Although shipment values for the industry for 1972 are not yet available from Commerce Department, actual prices received by producers are believed to have declined slightly. We have assumed an average industry plant price of \$245 per ton in 1972 for our profitability estimates.

For the period shown, actual prices have varied very little. The static price pattern reflects low demand growth, competition from imports, the availability of substitute materials for derivative products, and an over-capacity situation in the industry. Static plant prices have been offset somewhat during this period by declining costs for the chromite ore. Bichromate producers are believed to have written favorable, long-term contracts for chromite ore. These contracts, however, will be phasing out over the next several years. Renegotiations will probably be at higher levels, reflecting both increased ore costs and higher ocean freights.



TABLE 34

ACTUAL VS. LIST PRICES FOR SODIUM BICHROMATE  
(Cents per Pound)

<u>Year</u>	<u>List Price</u> <sup>1</sup>	<u>Actual Price</u> <sup>2</sup>
1960	13.00	12.74
1961	13.00	12.03
1962	13.00	12.78
1963	13.00	12.02
1964	13.00	12.00
1965	13.00	11.67
1966	14.00	12.69
1967	14.00	12.23
1968	14.00	11.95
1969	14.00	11.85
1970	15.00	12.02
1971	16.00	12.42
1972	16.00	Not available
1973	17.25	Not available

<sup>1</sup>Granular, bags, carlots, truckloads, works.

<sup>2</sup>Calculated from U.S. Department of Commerce reported value and quantity of shipments.

E. POTASSIUM CHROMATE AND BICHROMATE

While sodium chromate and sodium bichromate are by far the major chromium chemicals, a number of other chromium compounds are also produced from chromite ore. These secondary chromium chemicals include potassium chromate and potassium bichromate, ammonium bichromate, and chromium potassium sulfate. There are no government data for any of these materials on an individual basis. Commerce Department does report on an annual basis the dollar value of shipments for "other chromium compounds." In 1971, the most recent year for which data are available, the shipments of other chromium compounds were valued, f.o.b. plant, at \$9.5 million. This dollar total has varied between \$9.5 and \$10.5 million for the last five reporting years.

Although potassium chromate and bichromate are the most important of the secondary chemicals, production of the potassium compounds in the U.S. only totals 3,000 tons annually. There are a variety of miscellaneous uses for potassium chromate and bichromate, the most important of which are pigments and reagent grade materials. Allied is the only U.S. producer of importance.

Potassium chromate and bichromate can be made by a process similar to that for producing sodium bichromate by substituting potassium carbonate for sodium carbonate in the raw material mix. However, potassium bichromate is normally made from sodium bichromate and potassium chloride. Estimated manufacturing costs for potassium bichromate are shown in Table 35. The sodium bichromate has been charged into the potassium bichromate process essentially at manufacturing cost. As indicated, total manufacturing costs were estimated at \$402.75 per ton. Assuming plant netback at \$475 per ton (the list price for potassium bichromate is 24¢ per pound) and GS&A at 5% of sales, the after-tax profit per ton is \$24 per ton. This would be equivalent to an after-tax return on sales of 5.0%.

TABLE 35

## ESTIMATED MANUFACTURING COST, POTASSIUM BICHROMATE

Production: 15 Tons/Day of Potassium Dichromate  
 Operation: 330 Working Days  
 Investment: \$2,400,000 (Estimated)

<u>Item</u>	<u>Units</u>	<u>US\$/Unit</u>	<u>Units/Ton</u>	<u>Cost</u> (US\$/Ton Product)
Raw Materials				
Sodium Bichromate	ton	212	1.2	254.40
(content in solution)				
Potassium Chloride	ton	35	0.7	24.50
Utilities				
Power	MKwh	15	0.3	4.50
Fuel	MMBtu	0.7	15	10.50
Water	MGal	0.1	10	1.00
Direct Labor				
Supervisors	man-hr	7.50	0.6	4.45
Operators	man-hr	5.00	3	15.00
Helpers	man-hr	3.75	3	11.25
Overhead	(100% Direct Labor)			30.00
Maintenance Labor				4.00
Maintenance Materials				4.00
Depreciation	(6.5% of Investment)			31.95
Tax and Insurance	(1-1/2% of Investment)			<u>7.20</u>
Total Manufacturing Cost				402.75

## III. IMPACT ANALYSIS--INITIAL STUDY PRODUCTS

## A. ALUMINUM CHLORIDE

## 1. Treatment Costs

As developed in the Development Document, water treatment costs for aluminum chloride producers total \$3.77 annually per ton of product for E.P.P., B.P.T., and B.A.T. This amount would apply to plants operating on a chlorine-rich basis to produce yellow aluminum chloride, which is preferred for the manufacture of some dye and pigment intermediates.

Aluminum chloride plants operating on either a stoichiometric or aluminum-rich basis would have less waste chlorine stack gas and therefore lower pollution abatement costs. At least one producer is able to manufacture and sell 28% aqueous aluminum chloride solution derived from its scrubber effluents.

## 2. Price Impact

The maximum treatment cost of \$3.77 per ton represents approximately 1.3% of the current selling price of aluminum chloride. Further, it is estimated that it will cost an additional 0.4% of the current selling price to concentrate the dilute scrubber solution for yellow aluminum chloride. Although capacity utilization (at about 65%), captive usage, and demand growth are relatively low, and therefore act as price increase constraints, these factors are outweighed by the low level of foreign competition, the absence of substitute products, and the existence of only a few products all with equal treatment costs. (All producers of yellow aluminum chloride will be faced with approximately the same water effluent charges.) Some level of price increase is therefore possible, and producers of aluminum chloride should be able to cover at least part of their added treatment costs. Any costs which could not be passed on as a price increase would have to be absorbed by the manufacturers.

## 3. Plant Shutdown Impact

No plant shutdowns are expected as a direct result of additional water pollution abatement costs. Given the moderate degree of integration, the fact that plants with a water pollution problem will have already made a large investment in air pollution abatement equipment, and a relatively high emotional commitment on the part of the aluminum chloride producers, the very low level of added cost for water treatment is too small to result in plant shutdowns.

## B. ALUMINUM SULFATE

### 1. Treatment Costs

Water treatment costs for nonexemplary aluminum sulfate plants are estimated to be \$0.93 per ton of product above existing B.L.P. treatment, or \$1.72 per ton total. This added cost will raise average treatment level to zero discharge of process or cooling water effluent, which in this case is equivalent to E.P.P. Additional investment for a 40 ton-per-day plant is estimated to be \$60,000.

The treatment process which will effect zero discharge involves clarification and additional pond settling of mud and digestion wastes, followed by recycle of process water. Depreciation and operating costs exclusive of power account for 46% and 23% respectively of total treatment costs.

### 2. Price Impact

Since there are no suitable substitute products, foreign competition is minimal, and market share is concentrated among several producers, water treatment costs will probably be passed on as small price increases. The amount of the increases, however, will vary with each producer's local competitive situation. Although before-tax treatment costs are small relative to product price, the cost per ton of product is highly dependent on plant capacity, which varies from 5,000 to 70,000 tons per year for individual facilities. Such a disparity in capacity will enable the large producer to cover his unit treatment costs with a smaller price increase than the small producer will require.

The nature of the aluminum sulfate market, however, will probably allow most smaller producers to continue operations at reduced profit levels. Many small plants have been located near paper mills in order to supply aqueous aluminum sulfate economically for paper manufacture. Despite higher unit production costs, a smaller plant can supply at a lower delivered cost than a larger, more distant plant can, due to the cost of transporting water solution. Aluminum sulfate is sold dried and bagged only where plants and customers are widely scattered, and the product must be transported long distances. It is anticipated, therefore, that larger producers will raise prices to cover their increased costs as fully as possible. Smaller producers will probably raise prices only to the point where they can still marginally undersell their larger, more distant competitors--a point which most likely will not permit the small producer to fully recover his costs, but which will allow continued operation at lower profitability. In any case, it is not expected that prices need be raised more than 5% due to water treatment costs.

### 3. Plant Shutdown Impact

Recent years have seen the closing of some small plants and a trend toward larger, more efficient facilities. As demand for aluminum

sulfate as a water treatment chemical increases, the trend toward larger plants should continue. A large scale shutdown of small aluminum sulfate facilities, however, is not expected to occur as the result of anticipated increases in water treatment costs.

A very few marginally profitable plants may shut down, but these plants probably would have shut down anyway as a result of competition from larger plants. These occurrences will most likely be limited to situations in which a small plant cannot raise prices enough to remain profitable, while still underselling a larger, more distant competitor, and added water treatment costs represent the final negative factor against continued operation.

Industry capacity should continue to be sufficient to supply demand, and no increase in imports, with accompanying detrimental effects on balance of payments, is anticipated.

## C. CHLORINE AND CAUSTIC SODA

### 1. Treatment Costs

As estimated in the Development Document, the cost of water treatment for a 175 ton-per-day mercury cell plant to achieve effluent conditions equivalent to B.L.P. is \$2.14 per ton of chlorine produced. B.L.P. was defined in the Development Document as reduction of mercury to less than 0.5 pounds per day. For the exemplary plant investigated, the same investment, and therefore the same cost, was sufficient to reduce mercury to E.P.P. standards, i.e., less than 0.15 pounds per day. An incremental cost of \$0.60 per ton of chlorine above E.P.P. was estimated for catalytic conversion of sodium hypochlorite to sodium chloride, bringing the mercury cell plant to B.P.T. control level. An incremental cost of \$0.86 per ton above E.P.P. was estimated to achieve zero discharge (B.A.T.) and involved B.P.T. treatment plus evaporation and reuse of sodium chloride.

Similarly, the Development Document has estimated that the unit cost (in terms of chlorine) to achieve B.L.P. standards for a 2300 ton-per-day diaphragm cell plant is \$0.038 per ton, the treatment being restricted to settling ponds. The incremental cost for this same plant over and above B.L.P. to achieve E.P.P. standards is \$0.254 per ton of chlorine. This same unit cost is estimated to achieve B.P.T., but the assumption is made that there are no incremental operating costs associated with B.P.T. because hydrochloric acid recovered is assumed equal to cost. There is an incremental investment of \$430,000 estimated above E.P.P. to cover the installation of the hydrochloric acid plant for the chlorine tail gas. Finally, the incremental unit cost above E.P.P. to utilize B.A.T. standards for this plant is estimated at \$0.52 per ton of chlorine.



As a percent of the estimated \$100.90 industry average revenue in 1972 per ECU (1.0 tons of chlorine plus 1.1 tons of caustic soda), the before-tax unit cost above B.L.P. and E.P.P. (which are equal) for the mercury cell plant is 0.59% for B.P.T. and 0.85% for B.A.T. The comparable ratio for the diaphragm cell plant is 0.25% for E.P.P. and B.P.T. and 0.52% for B.A.T. Compared to the average industry profit margin of \$4.12 per ton for mercury cell plants (estimated in the initial study project) the incremental after-tax cost for B.P.T. in the mercury cell plant represents 7.3% of unit profits while B.A.T. represents 10.4% of industry profits. The comparable figures for the diaphragm cell plant (using \$4.33 per ton as average unit profit) are 2.93% for both E.P.P. and B.P.T. and 6.03% for B.A.T.

## 2. Price Impact

Chlorine/caustic producers have the theoretical option of attempting to recover water treatment costs through price increases for chlorine and/or caustic soda. In our judgment, the opportunity for defraying some or all the water treatment costs through higher chlorine prices is better than via raising caustic soda prices. Both capacity utilization and captive usage are atypically high on average for chlorine. Demand growth is good (at 6% per year) and foreign competition is non-existent. Although there are a relatively large number of producing companies (approximately 30), the water pollution abatement costs faced by mercury plants are not significantly different than those for diaphragm plants. The difference is insufficient to put the mercury plants at a significant disadvantage if prices were to be raised only to cover the water treatment costs experienced by diaphragm cell plants.

More severe constraints exist for price increases in caustic soda. Except for periods of abnormally low chlorine demand (e.g., that experienced in the 1970-71 recession), caustic soda has usually presented a disposal problem to most chlor-alkali producers. Because normal caustic soda demand growth has been insufficient to match caustic soda supply (which, in turn, is a function of chlorine demand), the excess caustic has been sold in competition with other sodium alkalis, notably soda ash, at distressed price levels. We expect a long-term continuation of the caustic soda excess and therefore continued downside pressure on caustic soda prices.

## 3. Plant Shutdown Impact

On the basis of the treatment costs estimated in the effluent guideline Development Document (and mentioned above), and based on the conclusion that most if not all of the nominal incremental costs for water treatment will be passed on through chlorine price increases, we foresee no plant shutdowns for producers who have already achieved B.L.P. However, an estimated 13% of the mercury cell plants have not yet made this investment. Instead of the \$0.86 per ton incremental costs mentioned above to reach B.A.T., these producers would be faced with a \$3.00 per ton cost. Some of these producers, assuming that they tend to be marginal plants, but probably no more than 5% of the industry (one or two plants), would be subject to shutdown.

## D. HYDROCHLORIC ACID

### 1. Treatment Costs

Treatment costs have been supplied for the chlorine burning process only, a method which accounts for at most 12% of total U.S. hydrochloric acid production. For a 40 ton-per-day chlorine-burning facility the total cost to apply B.A.T. is \$0.30 per ton of product (100% HCl), and the incremental cost above B.L.P. is \$0.05 per ton. The treatment process involves neutralization of weak acid effluent which is generated only during plant startup. According to the effluent guideline Development Document there is no steady-state waterborne effluent.

Additional investment required for B.A.T. for the 40 ton-per-day plant is only \$5,000. Depreciation and operating costs exclusive of power account for 35% and 47% respectively of the total annual treatment cost of \$4,250.

By-product production of hydrochloric acid from hydrocarbon chlorination (which accounts for 88% of total production) was not covered in the effluent guideline Development Document. The effluent guideline Development Document indicated, however, that there are no water treatment costs directly attributable to by-product production.

### 2. Price Impact

Due to its overwhelming preponderance of production capacity, the by-product route controls hydrochloric acid supply and prices. By-product acid will not have to bear the direct water treatment costs which burning plant acid will; hence, it is not anticipated that the treatment costs incurred by a small industry segment will be passed on as general price increases. The likelihood of no increase is further supported by the presence of many producers holding fragmented market shares and the fact that, despite a recent trend toward a more balanced supply/demand situation, production has exceeded consumption by as much as 32% since 1961. This situation has been brought about by by-product acid supply being a function not of hydrochloric acid demand, but of the non-related demand for chlorinated hydrocarbons and has had a strongly depressing effect on hydrochloric acid prices. The decreasingly small portion of the industry which is faced with water treatment costs, therefore, will be hard pressed to seek relief in the form of price increases and will be forced to absorb these costs.

### 3. Plant Shutdown Impact

Only those direct producers not in a chlor-alkali complex face the possibility of plant shutdown as the result of water treatment costs. The weak acid waste stream from direct production in a complex can be used to neutralize caustic waste from other parts of the complex, and the producer essentially incurs no waste treatment cost on hydrochloric acid.

There is only one known isolated, direct burning plant in the country, and it is located near a larger chlor-alkali complex which provides a readily available site for waste acid disposal at nominal cost. The fact that there are no direct burning hydrochloric acid plants unable to dispose of water wastes at nominal cost leads us to conclude, therefore, that water treatment costs will not directly result in shutdowns of direct-burning hydrochloric acid plants.

#### E. HYDROFLUORIC ACID

##### 1. Treatment Costs

As estimated in the effluent guideline Development Document, total treatment costs for a 40 ton-per-day hydrofluoric acid plant to achieve E.P.P., B.P.T. and B.A.T. are \$4.04, \$4.89 and \$12.95 per ton, respectively. Costs for B.L.P. were estimated at \$3.57 per ton. Annualized costs to bring the industry to E.P.P., B.P.T. and B.A.T., respectively, from B.L.P. therefore would amount to \$0.47, \$1.32, and \$9.38 per ton. As a percent of the estimated average industry's 1972 selling price of \$370 per ton, the annualized treatment costs for E.P.P., B.P.T. and B.A.T. would be 0.13%, 0.36% and 2.54%, respectively.

The initial study project suggested a range for after-tax profitability on sales of 4% to 10%. Taking 5% as average, the after-tax profit margin on a \$370 netback price would be \$18.50 per ton. The after-tax treatment cost as a percent of this profit margin for E.P.P., B.P.T. and B.A.T. is 1.30%, 3.57% and 25.4%, respectively. New investment in treatment facilities for E.P.P., B.P.T. and B.A.T. as a percent of net fixed plant investment is 0.60%, 1.00% and 1.50%, respectively.

##### 2. Price Impact

Conditions in the hydrofluoric acid industry are such that price increase constraints are low. Specifically, there are no economically viable substitute products for hydrofluoric acid in its major end-use applications. Captive usage is exceptionally high at about 75% of current consumption. Similarly, plant utilization is high at nearly 85% of the 392,000 tons of in-place capacity at the end of 1972. Demand growth is strong at 5% to 7% per year. Imports have been negligible so that there has been no threat of foreign competition. (Imports of hydrofluoric acid from Mexico will very probably increase in the future, however. Four U.S. companies have announced plans to build acid plants in that country with the apparent intent--initially at least--of using the acid captively for U.S. derivatives manufacture. There is the long-term possibility that increased pressure will be brought to bear by Mexico for manufacture of the derivatives of hydrofluoric acid in Mexico as well.) The price elasticity of demand for hydrofluoric acid is low. Market shares are relatively concentrated with two producers, Allied and Du Pont, accounting for more than 50% of capacity.

All of the foregoing considerations suggesting little or no constraint on price increases by far outweigh the two identified conditions tending to constrain price increases, viz. the relatively large number of producers (nine) and the fact that price is the primary basis for competition. Moreover, the magnitude of the price increase necessary to defray treatment costs even for B.A.T. (2.54% of the estimated industry selling price) is less than one-half cent per pound.

##### 3. Plant Shutdown Impact

Since we have concluded that the industry would be able to pass on the treatment costs through price increases we must also conclude that there will be no plant shutdowns on the basis of the treatment costs provided us. The magnitude of these treatment costs on an after-tax basis as compared with industry profitability and cash flows and the magnitude of the treatment investment compared with net fixed investment for the industry support this conclusion. Moreover, industry conditions do not suggest the possibility of plant shutdowns. The industry is heavily integrated to downstream products (as inferred from the high captive usage), there are no overwhelming additional environmental costs to be defrayed and producers have an emotional commitment to the product.

#### F. HYDROGEN PEROXIDE

##### 1. Treatment Costs

Based on the information developed for hydrogen peroxide in the effluent guideline Development Document, treatment costs to achieve B.A.T. are small relative to average selling price. For the electrolytic process, a process used by only one U.S. plant, the annual incremental treatment cost above E.P.P. and resulting in zero discharge would be approximately \$0.39 per ton, or 0.07% of the current average selling price of about \$596 per ton. The organic process, which is employed by five plants, leads to somewhat higher incremental costs for water pollution abatement. The incremental annual cost to achieve zero discharge via this process is \$0.86 per ton. This added cost is also relatively small (0.14%) compared to the average selling price of hydrogen peroxide.

##### 2. Price Impact

Although the potential impact on prices from water pollution abatement costs is small, producers of hydrogen peroxide may have difficulty in passing even these nominal costs on to customers through a price increase. The concentrated nature of the industry and the low level of substitute products are factors which would normally make it possible for producers to pass on increased costs, but the low level of capacity utilization (ca. 70%), low captive use (ca. 30%), some pressure on prices from foreign competitors, and differences in manufacturing costs due to plant size and processes used, are all factors which will make difficult any move to pass on the added treatment costs.



### 3. Plant Shutdown Impact

On the other hand, plant shutdowns as a direct result of such relatively small added water pollution abatement costs are also unlikely. The added costs may put some additional economic pressure on those producers whose plants are small and thus suffer diseconomies of scale. Additional plant shutdowns may occur as a result of normal economic forces, and thus smaller and/or older plants may be closed or placed on standby as capacity is adjusted to current demand.

There has been a trend in the industry to phase out the electrolytic plants, the economics of which are unfavorable compared to those operating by the organic process. The lower incremental cost for the electrolytic plant to achieve zero discharge may retard, rather than hasten, the decision to close this plant.

### G. LIME

#### 1. Treatment Costs

There are no waterborne wastes from the lime manufacturing process, and some plants (about 25% of the industry) have no waterborne wastes at all. According to the effluent guideline Development Document, those plants which do have waste-bearing water effluents are those which use wet scrubbing of gaseous effluent to remove entrained dust. While no costs were developed in the effluent guideline Development Document for wet scrubbing or treatment of scrubber effluents, the cost of installing a dry collection system (thereby avoiding waste-bearing water effluent) in a plant of 108,000 tons-per-year capacity was estimated at approximately \$1.28 per ton annually. This cost of \$1.28 per ton is taken as the maximum cost for zero discharge of waterborne wastes. It is recommended in the effluent guideline Development Document that water scrubbing and elimination of waterborne wastes be used whenever the total cost of such treatment is less than \$1.28 per ton. One large plant plans to install a recovery system on the wet scrubber waste stream, the cost of which will be covered by product value obtained.

#### 2. Price Impact

The annual treatment cost of \$1.28 per ton for lime producers not currently using dry collection techniques represents a significant added cost relative to the average plant price for lime, which is approximately \$16.00 per ton. A price increase of 8% would be required on lime produced at these plants to cover the maximum cost of water pollution abatement. Given a situation in which some lime producers will incur these costs while others will not, a price increase of this magnitude would only be tenable in a captive or quasi-captive situation in which a lime substitute (such as limestone in agricultural use) was not available, in which lime from another source could not be obtained at a lower (i.e., existing) price level, and in which the price increase could be passed on or absorbed by the lime consumer. In view

of the nature of the lime industry, the large number of plants widely scattered throughout the country, and the competitive nature of industries using lime, such a situation is unlikely. A more probable situation would be one in which a lime producer using dry collection techniques, and not faced with increased water pollution abatement costs, would supply lime, on a freight-equalized basis, which could be priced lower than that supplied by a lime producer currently equipped with wet scrubbers. In summary, depending on the local supply/demand balance, a few plants may be in a position to pass on nearly all of the added treatment cost, many others only a fraction of the additional cost, and still others will be unable to pass on any added cost at all. Chances for success of some attempt to raise prices by affected lime producers will be improved by currently high capacity utilization and by forecasts of future growth.

### 3. Plant Shutdown Impact

According to information developed in the effluent guideline Development Document approximately 25% of all lime plants are equipped for dry bag collection of particulates. It is also reported that recovery of product which would otherwise be lost offsets the annual pollution abatement cost. The remainder of the industry has plants which use wet scrubbing, electrostatic precipitation, or some other method of dust control. Of the plants using wet scrubbers, only those classified as commercial (as opposed to captive) plants have been identified in the initial study project. These plants represented approximately 25% of the commercial plants identified in the study, and are the plants most likely to be affected by the implementation of more rigorous standards for waterborne wastes.

Typical profitability levels in the lime industry are reported to be from 4% to 6% of average selling price. At approximately \$16.00 per ton, this would mean a maximum after-tax profit per ton of slightly under \$1.00. Thus, if none of the added cost could be passed on, a producer forced to absorb up to \$0.64 per ton after tax for water pollution abatement, would be left with less than half his normal profit from the sale of lime. Such a cut in profit levels for some producers could be the determining factor in a plant shutdown decision.

On this basis, we would expect that from four to ten plants may be closed. Since average employment in the lime industry is 35 persons per plant, this number of plant closings would mean that from 140 to 280 persons could be displaced. Fortunately, most plants having wet scrubbers are located reasonably close to urban areas and therefore in areas with potential employment alternatives.

### H. NITRIC ACID

#### 1. Treatment Costs

As reported in the effluent guideline Development Document, there are no direct waterborne process wastes and usually no waterborne wastes from air pollution abatement procedures in nitric acid manufacturing.



However, minor contamination of aqueous plant effluent may result from leaks, spills, and washdowns. It is also reported that 95% of the industry plants are at B.L.P. and that an incremental annual cost of \$0.22 per ton would be required to install B.A.T.

It should be pointed out that these treatment costs, as developed in the effluent guideline Development Document, apply only to producers of commercial grade nitric acid (up to 70% concentration), and that the costs do not cover treatment of waterborne wastes from ancillary (cooling tower and boiler blowdown) effluent streams. In addition, nitric acid water treatment costs were assumed to be the same as those for sulfuric acid, since nitric acid cost figures were not available.

## 2. Price Impact

Approximately 90% of U.S. nitric acid production is captively consumed; the remaining 10% is typically offered for sale at a considerable discount from list price through long-term negotiated contracts. Based on dollar value and tonnage of 1971 shipments and interplant transfers, as reported by the U.S. Department of Commerce, the average selling price for nitric acid was \$67 per ton. The reported maximum treatment cost for nitric acid, at \$0.22 per ton, is approximately 0.3% of this average selling price. With both relatively low capacity utilization (ca. 75%) and demand growth, and with price as the main basis for competition, an across-the-board price increase to cover full incremental treatment costs is unlikely. The ability of individual producers to raise prices will depend on the competitive situation within each local market. However, some plants will undoubtedly be forced to absorb most of the added water treatment cost.

## 3. Plant Shutdown Impact

While some nitric acid plants may be shut down over the next several years as a result of normal economic forces, it is unlikely that the impact of added water pollution abatement costs, as developed in the effluent guideline Development Document, will be a significant decision factor. Plant shutdown decisions will more likely be based on such factors as low local capacity utilization, technological obsolescence of older plants, and the much higher cost of air pollution abatement.

## I. SULFURIC ACID

### 1. Treatment Costs

Water treatment costs were estimated for plants using both sulfur burning and refinery acid sludge, which together account for 82% of all sulfuric acid plants. B.A.T. costs for sulfur burning were estimated at \$0.12 per ton of product and for sludge regeneration at \$0.50 per ton in both cases as increments above B.L.P. costs. For a 140,000 ton-per-year sulfur burning plant water treatment facilities investment is

\$110,000, representing 3% of existing net plant investment. A 262,000 ton sludge plant, however, would require an additional investment of \$1.15 million or 45% of existing net plant investment. The burning plant's water treatment operating costs are estimated at \$24,000 per year, of which two-thirds is depreciation, with no direct operating or power costs. The sludge plant, on the other hand, will incur annual costs of \$197,500 for B.A.T., with depreciation accounting for \$125,000 and operating costs exclusive of power amounting to only \$10,000. The treatment process in both plants entails neutralization of weak acid and isolation and containment of suspended solids.

## 2. Price Impact

We believe that water treatment costs can be passed on as a price increase. The amount and conditions for increase, however, are different for the two types of plants covered. Sulfur burning plants, the majority of which produce acid for non-refinery use, should incur water treatment costs which amount to only 0.6% of present selling price. Since these plants are concurrently encountering substantial air pollution control costs, it is expected that the relatively nominal water treatment costs will be passed on as part of joint air/water pollution control costs. Exact amounts of price increases will be dependent on local competitive conditions and the total amount of joint treatment costs to be passed on.

Refinery sludge plants, however, are in a special situation in that they are performing a service primarily for petroleum refiners who have no economical alternative for waste acid disposal. One sludge acid plant frequently handles the acid sludge streams of several refinery complexes since it is not economical for any but the largest refineries to have their own acid plants. Due to the sludge plant's higher investment and operating costs, higher prices are artificially maintained to provide the sludge operator with a profit equivalent to burning plants. In addition to air pollution costs comparable to those of sulfur burning, it is anticipated, therefore, that all of the water treatment costs, which amount to 10% of current selling price, will be passed on to refiners as price increases. Only the largest refiners will have the option of constructing their own sludge plant rather than accept higher prices.

## 3. Plant Shutdown Impact

Plant shutdowns due to water treatment costs alone are unlikely except for some sludge plants. For most non-sludge plants water treatment costs are not of sufficient magnitude to be the direct cause for plant shutdown. Some refinery sludge plants (no more than three or four) however, may face shutdown as a result of two special situations. In addition to returning fresh acid to local refineries, most sludge plants sell regenerated acid to commercial markets with the percentage of commercial business ranging from 10% to 100%. Since sludge producers face higher water treatment costs, the occasional producer dependent on a large percentage of commercial demand will be at a competitive disadvantage to the sulfur burning producer. The sludge

producer must cover high fixed costs through high capacity utilization, a condition which could be difficult to maintain if competitive burning plants under-price the sludge manufacturer. Due to water treatment costs, therefore, a sludge producer may face reduced profitability in the commercial market, either through reduced sales margins or through smaller capacity utilization, sufficient to warrant shutdown.

The other problem facing the sludge producer is the possibility of a refinery switching to captive sludge acid regeneration. This action is not likely since only a few refineries are large enough to economically operate their own acid regeneration plants. In addition, multi-site refiners may be reluctant to antagonize sludge producers by going to captive acid regeneration at one location while continuing to utilize the sludge converter at another site.

#### IV. IMPACT ANALYSIS--MAJOR STUDY PRODUCTS

##### A. CALCIUM CARBIDE

###### 1. Treatment Costs

The calcium carbide manufacturing process has no direct waterborne wastes, the only sources of effluent contamination being cooling tower blowdown and ion exchange requirements. One producer of calcium carbide uses the dry bag collection technique for air pollution abatement and has no significant water pollution abatement costs. The value of material recovered affects treatment costs in this case. Another producer, not yet having installed air pollution abatement equipment, is understood to be considering the dry bag approach.

The remaining two producers of calcium carbide, using water scrubbing for air pollution abatement, and representing approximately 85% of industry capacity, would have to isolate the scrubber effluent, remove suspended solids, and further treat the water before discharge. The annual operating expenses for such a scrubber effluent system are sufficiently large relative to after tax net income to make installation of a dry bag collection system--which, according to the effluent guideline Development Document, pays for itself from collection and recycling of raw materials and product--attractive even to those producers who have already installed scrubbers. For a small (50,000 ton per year) plant, the investment in wet scrubbers would be approximately \$54,000, or 1.4% of net fixed investment. The annual treatment costs before tax, would be approximately \$1.94 per ton.

The waterborne wastes from conversion of calcium carbide to acetylene are significant, and may have an additional impact on those plants at which acetylene is produced. We have not been provided with costs for the treatment of effluents which result from acetylene manufacture.

###### 2. Price Impact

Producers of calcium carbide using air bags for air pollution abatement will have no added costs for control of waterborne wastes. Producers using water scrubbers and choosing to continue their use, thereby incurring water treatment costs of \$1.94 per ton, or 2.2% of the estimated \$90 per ton average selling price, would have difficulty in passing the added cost on to consumers. Price increase constraints for calcium carbide are strong, and in view of available substitutes, current overcapacity, and a declining market, any price increase would only serve to further reduce demand.



### 3. Plant Shutdown Impact

While continued plant shutdowns may be expected as a result of economic forces over the next several years, the effect of water pollution abatement costs related to the manufacture of calcium carbide are expected to be relatively small. As is the case with many of the other chemicals in this study, air pollution abatement costs are considerably larger than those for control of waterborne wastes. Thus, the marginal plants have already been culled as a result of air pollution abatement impact, and those remaining plants which have not installed dry collection systems, either have sufficient commitment to bear the marginally small additional cost of scrubber effluent treatment, or to make the initial investment in a reportedly profitable air bag system. In the worst case, that of a contract supplier operating at the break-even point, it is estimated that annual cash flow from depreciation would cover annual water treatment operating expenses.

Calcium carbide plants which immediately convert their product to acetylene gas have the additional problems of handling the calcium hydroxide produced as a by-product. Water pollution abatement costs relating to acetylene production have not been supplied to us by EPA and it is beyond the scope of this report to assess the impact of these treatment costs. In general, however, acetylene producing calcium carbide plants tend to be captive or contract suppliers of calcium carbide acetylene.

Finally, as described in an earlier section of this report, the calcium carbide industry faces a continued declining market due to causes unrelated to environmental pollution abatement. In the normal product life cycle, calcium carbide seems to be well beyond maturity as more economical substitute products continue to gain a larger and larger market share.

### B. SODIUM SULFATE

#### 1. Treatment Costs

Treatment costs discussed in the effluent guideline Development Document pertain only to sodium sulfate produced as a by-product of sodium bichromate manufacture. These producers collect, dry, and sell the by-product, and reportedly have no waterborne wastes or treatment costs attributable to sodium sulfate.

Production of sodium sulfate as a by-product of sodium bichromate represents approximately 10% of total U.S. production. The most important source is recovery from natural brines, followed by production as a rayon and cellophane by-product.

#### 2. Price Impact

With no water pollution abatement costs assigned to sodium sulfate as a sodium bichromate by-product (chrome cake) no effect on

prices is expected for this product. It is unlikely, however, that a sodium sulfate price increase could be sustained in view of the high level of substitute products, foreign competition, excess capacity and a static or declining market.

### 3. Plant Shutdown Impact

Zero water treatment costs for producers of chrome salt cake mean no plant shutdowns. The bulk of U.S. sodium sulfate production is by producers for which no treatment costs have been developed, and therefore the impact of federal water pollution control costs on most producers of this chemical is beyond the scope of this report.

### C. TITANIUM DIOXIDE

#### 1. Treatment Costs

##### a. Sulfate Process

Two separate treatment approaches for sulfate process plants, acid neutralization and acid recovery, were discussed in the effluent guideline Development Document along with their respective costs. To utilize B.A.T. for a 42,000 ton plant, total treatment costs for neutralization are estimated to be \$98.09 per ton, or 17.2% of current selling price, and for acid recovery \$50.48 per ton, representing 8.9% of selling price. The investment in treatment facilities via either method is large--\$11.5 million for neutralization and \$5.5 million for acid recovery. These amounts represent respectively 55% and 26% of existing net plant and indicate the sizeable investment relative to existing plant required.

In the case of neutralization zero discharge treatment consists of solids settling, full neutralization of the waste acid streams, and the demineralization and recycle of process water. Annual costs amount to \$4.12 million of which \$2.35 million are operating and maintenance costs exclusive of power, and \$1.15 is depreciation. The acid recovery process involves recovery and recycle of strong acid waste plus neutralization and pond settling of the remaining effluent. Annual costs for acid recovery are significantly less than those of neutralization and amount to \$2.12 million. At \$445,000, or 21% of the total, energy costs are high relative to the neutralization option. Operating and depreciation costs amount to another \$850,000 and \$550,000, respectively.

A major item of concern raised in industry interviews was the technical feasibility of the acid recovery option. For a number of years the industry has been attempting without success to develop an acceptable acid recovery procedure. Since treatment costs could be only one-half of those for neutralization, the EPA-sponsored research in this area is being watched with interest, but with considerable skepticism. Due to the uncertainty of successful development of acid recovery technology, therefore, our sulfate process water treatment cost impact analysis will be based on the neutralization method alone.



Water treatment costs for B.P.T. are not significantly lower than for B.A.T. For the neutralization method, investment drops only to \$10 million and annual costs amount to \$3.51 million, or 85% of B.A.T. costs. The last incremental step to B.A.T., therefore, is not significantly more expensive than full neutralization, and will probably not affect price increase/plant shutdown decisions significantly.

#### b. Chloride Process

Water treatment costs for chloride process wastes are estimated to be significantly less than those for the sulfate process. B.A.T. can be attained at a cost of \$66.79 per ton for a 25,900 ton plant, which is a typical size plant in the industry. Total additional investment in treatment facilities for this plant is \$5 million, which represents 23.5% of existing net plant.

B.A.T. annual treatment costs total \$1.73 million, of which operating and maintenance costs exclusive of power account for \$890,000 and depreciation another \$530,000. The treatment process required to reach this level involves chemical neutralization of waste acid streams, thickening and land dumping of sludges, and removal of dissolved chlorides and sulfates through evaporation and recycle of process water. B.P.T. treatment, which is the same as E.P.P. and does not involve soluble chloride and sulfate removal, is considerably less costly than B.A.T. At \$4 million and \$1 million, treatment facilities investment and annual operating costs respectively are 75% and 58% of corresponding B.A.T. figures. B.P.T. investment requirements and operating costs, therefore, are lower for chloride producers, both in absolute terms and in comparison with B.A.T. requirements.

#### c. Barging and Deep-Welling

Currently both chloride and sulfate wastes are being barged to sea by several producers. Sulfate barging involves deep sea dumping of strong acid, sludge, and metallic sulfate wastes and costs \$8-10 per ton of product. Chloride waste barging consists of ocean dumping of strong acid and metallic chloride and oxide wastes, and costs are \$5-10 per ton of product. Considerable pressure is being brought to bear by private groups to stop ocean dumping, and the future of this alternative is very uncertain. Use of barging is limited for the most part to those plants located on the coasts, and it represents a significant cost advantage over chemical treatment options.

Deep-welling is currently being used by at least one producer to dispose of chloride process wastes. Geological conditions limit deep-welling to certain parts of the country; thus, this method is not possible for all producers. Costs range from \$2 to \$5 per ton of product, again significantly lower than chemical treatment costs. As in barging the future of deep-welling is clouded due to unresolved questions as to the effects of deep-well wastes on surrounding water

table structures. Clearly, however, if barging or deep-welling is allowed to continue by EPA, the producers fortunate enough to be able to utilize either method will incur significantly lower water treatment costs than those companies having to employ chemical neutralization methods.

#### 2. Price Impact

It is most probable that some part of water treatment costs would be passed on as price increases. There are several major reasons for this likelihood. In the face of a strong demand which is projected to continue for several more years, capacity will remain strained through at least 1975 when additional production facilities should come on stream. The industry is presently at 100% of practical capacity and is allocating product to customers. Secondly, there are no known substitute products which match titanium dioxide for cost effective hiding power. Foreign competition for the foreseeable future will be minimized through recent currency devaluations, the tight supply situation present in Europe, and the fact that European producers are themselves beginning to feel pollution control pressures. Lastly the water treatment costs estimated for the titanium dioxide industry are among the largest encountered for any chemical in this study. Pre-tax B.A.T. costs account for fully 16.8% of sales price for sulfate pigments, and 11.3% of sales price for chloride pigments. Applying these costs against our estimates of industry profitability, it becomes apparent that price increases would be necessary to avoid negative profitability as a direct result of water treatment costs.

At the present time the differential between sulfate and chloride process treatment costs poses a complication in assessing the magnitude of price increases for titanium dioxide pigment. The chloride producer, faced with treatment costs for B.A.T. of \$0.033 per pound can obtain relief with a smaller price increase than the sulfate producer, who must cope with treatment costs of nearly \$0.05 per pound. Industry sources believe that, for the next two to three years, the supply/demand situation for titanium dioxide pigment would permit sulfate producers to raise prices more than chloride producers in order to recover their higher water treatment costs. Such a differential could not exceed \$0.01 to \$0.02 per pound, especially in view of the chloride pigment's superior performance in many applications, and it could not be sustained if additional capacity were brought on stream or if imports become more price-competitive. It is most probable that chloride producers would raise prices only enough to cover their own treatment costs, since raising prices by the same higher amount as sulfate producers may require would increase chloride process profitability to the point where new competition would likely be encouraged. B.P.T. treatment would lower the absolute treatment costs for both chloride and sulfate producers, but would also widen the differential in treatment costs for the two processes by almost \$0.007 per pound. The sulfate producer would thus be placed at an even greater disadvantage relative to the chloride producer.

### 3. Plant Shutdown Impact

The probability of plant shutdown is difficult to assess because of the uncertainty in the amount and duration of price increases, and the resultant profitability effects, based on water treatment costs. Sulfate producers are most likely to face plant shutdown decisions because of the age of most sulfate plants and the extremely high treatment facilities' investment projected. Confronted with an investment amounting to 50% of existing net plant, and the prospect of long-term negative profitability if prices cannot be raised to fully cover treatment costs, industry sources report that a shutdown decision would probably be made. This decision would be complicated by the prospect of continued positive cash flow from full capacity operation in the presently strong market. However, the recent closing of a chloride facility by NL Industries, even in the face of the presently strong market, indicates that producers might shut down an operation burdened with continued negative profitability.

We conclude, therefore, that over the long range one or two smaller sulfate facilities might shut down as a result of water treatment costs. The actual closings could be delayed as the producers attempt to compete in the favorable pigment market as long as possible, but we feel that the magnitude of investment and annual costs would eventually make shutdown a necessity. The chloride producers will probably be less affected by water treatment costs and we do not anticipate any chloride facility closings as the direct result of these costs.

### 4. Impact Analysis Sensitivity

We have assessed the sensitivity of our impact conclusions for titanium dioxide if treatment costs are higher than those estimated in the effluent guideline Development Document. We conclude that if costs are in fact understated by a factor of four, the impact on the titanium dioxide industry will be severe and substantial plant shutdown could be expected especially among sulfate producers.

With a fourfold increase in treatment costs over those shown in the effluent guideline Development Document, pre-tax costs for B.A.T. would be \$0.12 per pound or 45.2% of present selling price for chloride pigment and \$0.19 per pound or 67.2% of present selling price for sulfate pigment. Impact on after-tax net income and cash flow is even more severe. B.A.T. treatment costs for chloride pigment are 948% and 136% of net income and cash flow respectively, and 932% and 261% respectively for sulfate pigment. B.A.T. costs would thus exceed both net income and cash flow, and plant shutdowns would be inevitable.

Implementing treatment procedures to use B.P.T. only would reduce the absolute magnitude of treatment costs, but would widen the differential between chloride and sulfate costs and subsequent impact

effects. B.P.T. costs pre-tax would be \$0.07 per pound, or 25.6% of selling price for chloride pigment, and \$0.16 per pound, or 57.2% of selling price for sulfate. Both chloride and sulfate pigment would show negative profitability, but chloride cash flow would remain positive (after-tax treatment costs of 78.6% of cash flow). Sulfate pigment, with after-tax costs representing 223% of cash flow, would continue to show negative cash flow. We conclude, therefore, that substantially higher treatment costs, even with B.P.T. treatment, would result directly in plant shutdowns, and that the sulfate producers would be more severely affected.

As pointed out earlier, it should be possible for producers to obtain relief by passing some of the treatment costs along as price increases. If costs are adjusted upward by a factor of four, however, it is doubtful that this new level of treatment costs could be passed on in full. While titanium dioxide has no equally cost effective substitutes at its present price level, a price higher than about \$0.40 per pound makes substitution by high brightness clays and other pigments economically attractive. Due to the surface properties it imparts, especially in paints, titanium dioxide will not be completely replaced, but its demand would be curtailed via substitution. A secondary limitation on the magnitude of potential price increases is price competitiveness of the final product in which titanium dioxide is used. Paint prices, for instance, cannot be raised substantially without losing business to other wall covering materials such as wallpaper or wood paneling. A titanium dioxide price of \$0.40 per pound would result in a \$0.15 per gallon increase in paint price, assuming 1.3 lbs. of titanium dioxide per gallon of paint and no substitution by cheaper pigments.

Passing on B.A.T. treatment costs in full would result in a price increase to the \$0.40 per pound range for chloride pigment and to nearly \$0.48 per pound for sulfate. We believe, therefore, that B.A.T. treatment costs would not be passed along completely. Passing on B.P.T. treatment costs in full will result in a more tolerable \$0.35 per pound price for chloride pigment, but will still leave sulfate pigment, at nearly \$0.45 per pound, susceptible to replacement by lower cost pigments. Sulfate producers would most likely be able to recover only \$0.07-\$0.08 per pound of their treatment costs via a price increase to \$0.36-\$0.37 per pound. In this situation, the industry would be operating with chloride producers fully recovering their costs and maintaining existing profitability and with sulfate producers operating with negative profitability and negligibly positive cash flow. We would expect, therefore, that even at B.P.T. treatment, price increases would not be sufficient to avoid major impact on titanium dioxide production, especially for sulfate pigment.



## D. SODIUM CHROMATE AND BICHROMATE

### 1. Treatment Costs

The effluent guideline Development Document has estimated treatment costs for a 164 ton-per-day sodium bichromate plant to achieve E.P.P., B.P.T. and B.A.T. at \$11.66, \$16.45, and \$16.45 per ton, respectively. E.P.P. control involves segregation and chemical treatment for chromium-6, followed by pond settling and discharge of clear effluent to surface water. B.P.T. involves evaporation to recover dissolved sodium chloride in addition to E.P.P. control. The incremental unit costs above B.L.P. (settling ponds estimated to cost \$0.26 per ton), therefore, are \$11.40 per ton for E.P.P. and \$16.19 per ton for B.P.T. and B.A.T.

As a percentage of the estimated 1972 industry selling price of \$245 per ton, E.P.P. costs amount to 4.6% while B.P.T. costs on an incremental basis amount to 6.6%. As compared to the estimated 1972 after-tax profit margin of \$18.50 per ton, the incremental cost to achieve E.P.P. effluent standards is 30.8%, while achievement of B.P.T. standards would represent 43.7% of 1972 unit margins.

### 2. Price Impact

On balance, factors constraining price increases in the sodium bichromate industry outweigh those factors suggesting that price increases are possible. Specifically, the high occurrence of substitute product for sodium bichromate derivatives, the tough foreign competition (including imports of sodium bichromate per se, as well as imports of derivatives such as chromic acid and chrome colors) and declining future demand all argue against the possibility of price increases. Moreover, abatement cost differences exist among the three producers. The exemplary plant, for example, has already achieved E.P.P. and need make only a relatively nominal investment to utilize B.P.T. These negatives outbalance those industry factors--viz. the small number of producers (three) and concentrated market share distribution--which would tend to make price increases possible. We conclude, therefore, that the full cost of water treatment control will not be passed on as price increases.

### 3. Plant Shutdown Impact

In view of the conclusion that additional water treatment costs will be absorbed, there is a possibility that one of the three sodium bichromate plants will be shut down. Full absorption of the treatment costs to achieve B.P.T. would represent very nearly a 50% reduction in after-tax unit profit margins. Moreover, there is the possibility that current margins will be reduced from 1972 levels (even without increased water treatment costs) by virtue of higher future chromite ore prices. The incremental investment (\$1.7 million)

for water treatment control is relatively high in comparison to the investment in existing plant. The three plants are isolated and could not achieve treatment economies with other company products. Finally, the industry faces in addition to water treatment investment both air pollution and above normal OSHA costs. With respect to the latter, the toxic nature of chromium will require safety measures beyond normal plant practices. Although on a superficial basis the industry is integrated both backward and forward, the raw material requirements--soda ash and sulfuric acid--are insufficient to justify continued operation on that basis alone. Similarly, the primary downstream derivative--chromic acid--is considered part (and a less important part) of the chromate operation. If the sodium bichromate plant were considered uneconomic, the chromic acid facility would be shut down as well.



## V. IMPACT ANALYSIS--ADDITIONAL PRODUCTS

In this section, we have provided: (a) summary comments of expected economic impacts on each of the additional products and (b) back-up commentary for the summary comments only on those critical points as indicated by the impact analysis matrix. Specifically these points were those: (a) which mitigated against the possibility of the producers' raising prices to cover the additional cost for effluent treatment; and (b) where treatment costs and estimated profitability were such as to affect a plant shutdown decision. As indicated by the commentaries for each individual product and the impact analysis matrix, we have tended not to comment on those individual factors which were not relevant to the impact judgment.

### A. SODIUM BICARBONATE

#### 1. Summary

We foresee no significant economic impact on the producers of sodium bicarbonate due to requirements to reach either exemplary plant practice, best practicable technology levels of treatment or best available technology levels. This conclusion is based on the extremely modest capital requirement and operating costs specified by the Development Document to reach necessary control levels and the apparent pricing flexibility available to the producers. The ability of the producers to raise prices over the past several years has been assisted by significant reductions in capacity at a time of relatively rapidly increasing demand. These capacity reductions were brought about by the closing down of two Solvay process sodium carbonate plants which served as sources of raw material for the production of sodium bicarbonate by these companies.

#### 2. Price Impact

As shown in the impact analysis matrix, the costs of effluent control are an extremely small proportion of the selling price. Increases in selling price in the past decade have been of such magnitude as to dwarf the control cost to insignificance. We foresee no reason that future price increases could not be effected to offset additional control costs and in fact, it would not even be noticed in the trend of rising prices. The list price for sodium bicarbonate in 1952 was at \$2.10 per hundred weight. This prevailed until 1967 when it was raised to \$2.55 per hundred weight. By 1966, it was again increased to \$2.80 per hundred weight and in 1969 to \$3.10 per hundred weight. By 1970, the price had increased to \$3.40 per hundred weight and by 1973 to \$4.40 per hundred weight.

The average price has quite probably been somewhat lower than the list price published for sodium bicarbonate. The average prices as

calculated from the current industrial reports of the U.S. Department of Commerce are, however, probably more misleading than list prices. This government data provides tonnage of finished bicarbonate shipped and the value. In 1971, this calculated to \$49.00 per ton. These "average" prices, however, are probably distorted by the relationship that exists between Church and Dwight and Allied Chemical. Church and Dwight markets both crude and high purity sodium bicarbonate manufactured by Allied Chemical in Syracuse, New York. The company also operates a sodium bicarbonate plant in Green River, Wyoming, to convert trona to sodium bicarbonate. The Government data may include shipments of crude product to Church and Dwight's plants, thus distorting the average price.

As shown in the impact analysis matrix, only a low captive usage and the relatively low demand growth would indicate on a theoretical basis the difficulty in raising prices. We do not believe in practice, however, that either one of these considerations will tend to limit future price increases so as to offset the modest cost of effluent treatment.

#### a. Capacity and Captive Consumption

Estimated producers capacities in 1973 are as follows:

Church and Dwight, Green River, Wyoming	100,000 tons
Church and Dwight, Syracuse, New York	100,000
Diamond Shamrock, Painesville, Ohio	28,000
BASF Wyandotte, Wyandotte, Michigan	36,000
	264,000 tons

These producers sell a great majority of their production of sodium bicarbonate for application in the manufacture of industrial or consumer products. The food industry takes 35-40% of the total bicarbonate shipments, rubber and chemicals take about another 20%, the pharmaceutical requirement is around 13%, and fire extinguishers about 12%. The remainder is used in the soap and detergent industry, textile, paper and leather industry. The major marketer, Church and Dwight, does account for some captive consumption through consumer sale of sodium bicarbonate under the Arm & Hammer brand.

The significance of the relatively low captive consumption in the price restraint is small when considered in the light of the small number of producers competing for the business and the relatively high capacity utilization. Capacity utilization has been assisted by both an increase in a recent growth of demand and, more significantly, by the shutting down in 1971 of a 23,000 ton per year plant of Olin Corporation and a 35,000 ton per year unit of PPG. Reportedly, these units were closed down because the Solvay process soda ash plants, which provided raw material for the manufacture of sodium bicarbonate, were uneconomical.

### b. Demand Growth

Sodium bicarbonate is a relatively mature product with only modestly increasing demand. The U.S. Department of Commerce current industrial report indicates shipments of sodium bicarbonate expressed as soda ash increasing from 100,000 tons per year in 1961 to 156,000 tons per year in 1971, or at an overall rate of 4 1/2% per year. The demand growth rate increased somewhat over the last five years to an average of 6% per year. No substantial change in the 10-year growth rate is foreseen for the remainder of the decade.

Growth in demand has been steady over the past decade with each year's requirements larger than the previous. There are no apparent or announced plans for significant expansion; therefore, the outlook for the foreseeable future is that capacity utilization will remain relatively high in spite of a modest growth in demand.

### c. Basis for Competition

Sodium bicarbonate like other commodity chemicals is sold on specification. The exception to this is the consumer sales of sodium bicarbonate under the recognized brand name. As indicated above, we believe that this is a relatively small proportion of total U.S. requirements.

Actually under present conditions, competition is probably not only on the basis of price but also on the basis of assured supply. Even during periods when the capacity was more significantly in excess of demand, this did not inhibit steadily increasing prices as described above.

### 3. Plant Shutdown Impact

The Development Document indicates annual treatment costs for a 100,000 ton sodium bicarbonate plant at \$2500 a year under current practices. To reach best practicable technology or best available technology conditions requires a total of \$4250 per year for the same plant. An increase of only \$1750 per year, therefore, is required to go from current conditions to the more stringent effluent controls foreseen. As shown in the impact analysis matrix, this is an extremely modest proportion of the estimated total after tax net income. As estimated, sodium bicarbonate producers at present price levels received an 8% after-tax return. Even should this estimate be significantly higher than actual practice, it is hard to imagine that the very modest additional cost requirements for effluent control would significantly affect any decision on plant shutdown.

#### a. Integration

We have classed the degree of integration as low chiefly because there is very little forward integration in the industry. In a practical

sense, there is a high degree of backward integration in the terms that Church and Dwight operates under long term commitments to Allied Chemical for the sale of sodium bicarbonate. The only non-integrated plant in the industry is Church and Dwight's facility in Green River, Wyoming, constituting about 40% of total capacity. This plant is operated on products supplied from Allied Chemical's trona facility at Green River. We assume that this facility is protected by a long-term contract with Allied and by the long standing relationship between Church and Dwight and Allied, whereby Allied has normally acted as the manufacturing partner and Church and Dwight the marketing partner for sodium bicarbonate.

### b. Emotional Commitment

Emotional commitment of the producers is hard to assess. We assume that Diamond Shamrock and BASF Wyandotte would have little commitment to the manufacture of sodium bicarbonate. Church and Dwight, however, has not only developed a consumer marketing franchise but sodium bicarbonate and sodium carbonate constitute the bulk of sales of Church and Dwight Company Specialty Chemicals Division.

### c. Ownership

As described, most of the capacity for the production of sodium bicarbonate is controlled by multi-industry concerns, Allied, Diamond Shamrock and BASF. All of these companies do have a variety of options for employment of capital. We do not foresee, however, that there are sufficient negative concerns indicating plant shutdowns so as to restrict the very modest investment required. The Development Document indicates that currently a 300 ton per day sodium bicarbonate facility has a \$10,000 investment in water pollution abatement facilities and this need only be increased to \$15,000 to meet all future effluent control standards.

## B. SOLAR SALT

### 1. Summary

In the solar evaporation process, seawater or salt lake water is concentrated by evaporation over a period of five years in open ponds to yield a saturated brine solution. After saturation is reached (approximately 30° Baume) the brine is fed to a crystallizer where sodium chloride precipitates leaving behind a concentrated brine solution (bittern) consisting primarily of sodium, potassium, and magnesium salts.

According to the Development Document the bittern solution, which contains all of the wastes from the process, is presently stored (ponded) at all facilities. Consequently, the solar salt industry is faced with no incremental costs to achieve zero discharge and there will be no negative impact on solar salt producers from new water



pollution abatement procedures. The Development Document estimates existing costs for bittern storage at the exemplary facility (annual capacity at very nearly 1 million tons) at \$2.34 per ton.

## 2. Price Impact

Although the question is academic, examination of some of the competitive factors impacting on the solar salt industry indicates that if there were incremental costs associated with water treatment, solar salt producers would be hard put to pass much if any of the costs on as price increases.

### a. Substitute Products

Solar salt is marketed as harvested (so-called "undried stack run") or further processed (via size classification and/or purification) before sale. When sold as such it competes with rock salt (valued F.O.B. mine at approximately \$3 per ton) primarily for chemical markets (basically chlor-alkali production). When purified and classified by particle size it competes with vacuum pan evaporated salt at unit values ranging between \$6 and \$40 per ton. Therefore, there is no other chemical that competes with solar salt as a direct substitute. The other sources of salt--particularly rock salt for which there are no waterborne wastes--are significant constraints on the solar salt producers to raise prices unilaterally. (The only exception might be the use of calcium chloride as a replacement for sodium chloride in highway snow and ice control, but even here the use of calcium chloride is complementary rather than substitutive.)

### b. Demand Growth

Although Commerce Department data for U.S. consumption of solar salt are not available, U.S. production of solar salt has exhibited a pattern of static to very slow growth. Actual production data for the last ten years in thousands of tons are as follows:

	<u>Thousands of Tons</u>
1972	1799
1971	1937
1970	1538
1969	1907
1968	1900
1967	1729
1966	1769
1965	1700
1964	1592
1963	1766

## c. Foreign Competition

U.S. solar salt producers have been under extreme competitive pressure from Mexican imports of solar salt. The bulk of U.S. solar salt production is in California and to a lesser extent Utah. In 1972, Mexican imports of solar salt totaled 1.25 million tons with a unit value of \$2.29 per ton. The competitive threat of low-cost Mexican solar salt also effectively constrains price increases by western U.S. solar salt producers.

### d. Abatement Cost Differences

Water pollution abatement costs for U.S. solar salt producers are equal to foreign competitors (in that they are zero) and better than equal (in that they are less) with respect to U.S. producers of evaporated salt.

### e. Price Elasticity of Demand

Increased prices for U.S. solar salt would result in reduced demand from consumers who have the option of increasing purchases of foreign solar salt or domestic rock salt.

## 3. Plant Shutdown Impact

With no new water treatment costs as indicated in the Development Document, there will be no solar salt plant shutdowns directly attributable to water pollution abatement measures. As indicated in the preceding paragraphs, however, if there were water treatment costs, solar salt producers would find it difficult to raise prices in order to pass on treatment costs.

## C. EVAPORATED SALT

### 1. Summary

The Development Document has estimated incremental water treatment costs for both B.P.T. and B.A.T. for evaporated salt producers at \$0.44 per ton. In comparison with the reported 1972 unit value for evaporated salt of \$26.94 per ton, the cost of water treatment represents 1.64% of sales value. This relatively nominal percentage in combination with competitive conditions in the industry wherein the only constraints against price increases are low captive usage (essentially zero) and modest demand growth (2.5% per year in the post-World War II period) leads to the conclusion that evaporated salt producers will be able to pass on the added cost of water treatment through higher prices. It follows, therefore, that plant shutdowns as a result of new water pollution abatement standards are unlikely.



## 2. Price Impact

The only factors acting as constraints against price increases for evaporated salt in our format are low captive usage and relatively low demand growth. For practical purposes, there is no captive usage at all by evaporated salt producers--all production is sold to merchant consumers. In the context of the evaporated salt market, however, this factor is not a strong constraint against price increases. Similarly, although demand growth has been low (approximately 2.5% per year in the post-World War II period) demand increases have been steadily upward on a year-to-year basis. Although the U.S. evaporated salt market has not been characterized by dynamic growth, it has experienced consistent growth. These two weak price increase constraining factors are outweighed by the following considerations.

### a. Substitute Products

There are few, if any, substitutes for evaporated salt in its major applications. The other primary forms of salt (rock or brine) don't compete with evaporated salt for most of its end uses.

### b. Capacity Utilization

Capacity data for U.S. evaporated salt manufacturing facilities are not available. It is reasonable to assume, however, that plant capacities and demand are in reasonable balance. We base this assumption on the predictable nature of year-to-year demand growth and the fact that the number of evaporated salt producers has not changed. That is, with no new market entrants to upset the supply position of existing competitors and with relatively few year-to-year upsets in the growth pattern, we assume that there has been a disciplined expansion of plant capacity in reasonable concert with market demand.

### d. Foreign Competition

Although Bureau of Mines data for salt imports are not segregated by type of salt, the identity of the importing country--and particularly the major importing countries--indicates that only nominal quantities of evaporated salt comes from foreign sources. The major importer of salt to the U.S. is Mexico, supplying almost exclusively solar salt. The next largest importer is Canada, almost all of whose salt exports to the U.S. are in the form of rock salt. The third largest importing country is the Bahamas which supplies solar salt exclusively. The unit value of total imported salt in 1972 was \$3.46 per ton, another indication that imports are comprised of the lower valued salt types, i.e., rock salt and solar salt.

### e. Abatement Cost Differences

There is no indication in the Development Document that there would be abatement cost differences between the various evaporated salt producers.

## f. Price Elasticity of Demand

As indicated by the absence of substitute products and the small percentage represented by evaporated salt of the total manufacturing cost in its applications, demand for evaporated salt is relatively insensitive to price.

### g. Basis for Competition

Although price is an important factor in marketing evaporated salt, there is opportunity for product differentiation through quality control, particle size control, and the addition of additives to impart desirable physical and nutritive characteristics for specific use industries. In addition, there is an opportunity and need to provide both technical and marketing service. The opportunity for product differentiation and to provide service to the user also makes nominal price increases possible.

### h. Market Share Distribution

Although individual company capacity data are not available (from which market share information could be inferred), it is probable that the three major salt producers--International, Morton, and Diamond Crystal--are also major evaporated salt suppliers. This would indicate a relatively concentrated market share distribution pattern.

## 3. Plant Shutdown Impact

Based on our conclusion that competitive conditions in the evaporated salt industry will allow producers to pass on the added costs of water treatment through price increases, no plant shutdowns would result from new water quality standards. The relatively high costs of water treatment in comparison with estimated profits (after tax costs equivalent to 13.7% of after tax profits for both B.P.T. and B.A.T.) and fixed investment (an investment in water treatment facilities equivalent to nearly 34% of existing plant investment for both B.P.T. and B.A.T.) suggests that producers would be motivated to recover the investment through price increases.

## D. SODIUM SILICATE

### 1. Summary

The cost of water effluent treatment indicated by the Development Document is small enough that, in an expected environment of relatively high capacity utilization, price increases may be effected to compensate for such increased cost. No plant shutdowns can be anticipated for sodium silicate plants to which the Development Document is applicable.

## 2. Price Impact

As indicated in the impact analysis matrix the price increase constraints relative to sodium silicate water effluent treatment costs are limited to the following.

### a. Capacity Utilization

While 1972 capacity utilization, at approximately 70% of installed capacity, is sufficiently low to contribute to a highly competitive environment, an environment in which price increases necessary to offset water effluent treatment costs might be difficult to achieve, there are indications that a major increase in capacity utilization will be effected over the next two years. After five years of static production volume, U.S. sodium silicate production increased 6% in 1972. And for the first seven months of 1973, production is 13% higher than for the same period of 1972. Thus capacity utilization in 1973 is likely to be 80% and less constraining relative to future price increases.

### b. Captive Usage

Sodium silicate is used captively in the production of fluid bed cracking catalysts, rubber reinforcing pigments, detergents, and for further processing to sodium metasilicate. However, many of the captive users also are merchant buyers, frequently on an "over-the-fence" long-term contractual basis. Such contracts tend to influence the marketing environment in much the same way as captive usage. Thus the low captive usage factor is augmented by the special contractual arrangements and is not a substantial constraint in the case of sodium silicate.

### c. Demand Growth

Sodium silicate production is recorded by U.S. Department of Commerce:

<u>Year</u>	<u>Production</u> (M Tons)
1967	613
1968	633
1969	657
1970	628
1971	628
1972	663
1973 (7 mo.)	416

As indicated under Capacity Utilization, demand was relatively static for the period 1967-72 and then increased sharply in 1972-73 because of household detergent consumption. The sharp rise in detergent consumption was initially motivated by local legislative restrictions

(city, county, state) on phosphate content. The household detergent manufacturers increased silicate content to compensate for phosphate reduction. In the face of an adverse marketing environment, phosphate manufacturers understandably made no plans to expand phosphate capacity. A shortage of phosphates then developed and the high energy requirements of phosphate furnaces probably precludes new furnace capacity in the short term and the long term. As a result the reduction of phosphate content in household detergents and expanded use of silicates is now directly attributable to both the legislative restrictions and the phosphate shortage. In other words, average phosphate content is lower than required to meet legislative restrictions because of phosphate unavailability.

The household detergent reformulation process, and attendant rise in silicate consumption, is not expected to carry beyond 1975, after which the growth in silicate demand should be no more than 2-3% per year. Thus, we have characterized demand growth in the impact analysis matrix as low.

### d. Basis for Competition

The primary basis for competition in marketing silicates is price. This does not mean, however, that price competition results in frequent changes of supplier pattern or price erosion. The marketing strategies of major producers depend to a significant degree upon market proximity to large consumers, proximity which frequently includes "over-the fence" transfer, and supply contracts. This tends to provide price stability and an opportunity to negotiate price increases necessary to compensate for increased manufacturing costs.

The above mentioned constraints are unlikely to be significant because the water effluent treatment costs provided by the EPA Development Document are no more than 1% of selling price.

## 3. Plant Shutdown Impact

In developing the environment for the plant shutdown decision in the impact analysis matrix, the conditions which might lead to a sodium silicate plant shutdown because of the cost of water effluent treatment are described below.

### a. Ratio of After Tax Treatment Cost to After Tax Net Income

Lacking current experience detail for after tax net income attributable to sodium silicate production and marketing, we assumed that 5% of selling price was reasonable for this class of inorganic chemical. More thorough economic analysis was not possible under the scope of our assignment. Based on the 1971 Department of Commerce unit sales value, the 5% after tax net income is \$4.30 per ton.



The EPA Development Document indicates the cost differential of achieving acceptable effluent treatment via exemplary plant practice as \$.40 more than base level practice. The differential over base level practice necessary to achieve best practicable technology or best available technology levels is \$.90. Thus the ratios of after tax treatment costs to after tax net income are 10% for E.P.P. and 20% for B.P. and B.A.T. Such an impact on profitability, if not recoverable through price increase, could contribute to a decision for plant shutdown.

#### b. Chemical Complex

Isolated plants are more likely to be shut down because of an inability to take advantage of common effluent treatment facilities. In general the locations of the sodium silicate plants are more influenced by the need for proximity to specific customers than by the advantages of including them in large chemical complexes.

#### c. Ownership

Because most of the sodium silicate production is owned by large multi-product chemical companies, plant shutdown decisions can be made on the basis of maximum return on investment with a multiplicity of choices. The shutdown of a single plant becomes less critical to the total operations of the corporation and is more readily made than would be the case if a dramatic reduction in total sales were attributed thereto.

### E. SODIUM METAL

#### 1. Summary

We expect little economic impact from the imposition of effluent controls to achieve E.P.P., B.P.T., or B.A.T. levels in the production of sodium metal. Sodium metal, produced by the electrolysis of molten sodium chloride, has by far its major application in the production of alkyl leads (tetraethyl and tetramethyl lead) for use in gasoline. The alkyl lead producers have integrated back to sodium metal and account for the great bulk of its production. The costs of effluent control specified by the Development Document, although a significant proportion of the probable profitability of producing sodium metal, are, we believe, a very much smaller proportion of the profitability associated with the entire operation of producing alkyl leads, including the manufacture of metallic sodium. If demand were to be sustained for alkyl leads, the relatively minor cost of effluent control for sodium manufacturing portion of the total process could either be absorbed by the manufacturers or, more likely, passed through to the purchasers of alkyl leads.

The total demand for alkyl leads will very probably decline significantly within the next three to four years. This will occur

chiefly because of the imposition of automobile emission control standards. This will reduce the demand for sodium metal and could quite possibly result in the shutdown of some sodium metal producing plants. It would not be reasonable, however, to attribute the plant shutdown to required investment and/or additional cost caused by meeting effluent control standards for metallic sodium. The plants would very likely close in any event with the substantial reduction in demand foreseen.

#### 2. Price Impact

Price increase constraints are not particularly meaningful applied to sodium metal because of the integrated nature of production. Producers of sodium metal account for over three-quarters of its total use in the United States. Most of the "price" therefore is a transfer price within a corporate enterprise. This transfer price could and most likely would be adjusted to take into account the higher manufacturing cost caused by imposition of effluent control standards on the manufacture of sodium metal.

#### a. Substitute Products

Sodium metal is primarily used in the production of tetraalkyl leads (tetraethyl and tetramethyl) which are used as gasoline additives for the prevention of knocking. This end use represented 83% of sales. Tetraalkyl lead production depends on sodium. These products have been put in gasoline for decades, and there is no substitute which is as satisfactory for improving octane rating per unit of cost. Nevertheless, certain aromatics may be used in the future because of emissions control standards affecting the use of leads.

Other uses for sodium include reduction of metals, especially titanium (6%), and manufacturing sodium peroxide (2%). Sodium metal receives severe competition from magnesium for use in metal reduction. Demand for sodium peroxide in pulp bleaching has decreased dramatically in recent years, losing markets to other chemical products such as hydrogen peroxide. Thus, for its major use sodium has little substitute product competition, but there is significant substitute product competition for minor uses of sodium.

#### b. Capacity Utilization

During 1969-1972 nationwide sodium metal manufacturing capacity was 189,000 short tons:

	<u>Tons/Yr.</u>
DuPont, Memphis, Tennessee	35,000
DuPont, Niagara Falls, New York	42,000
Ethyl, Baton Rouge, Louisiana	45,000
Ethyl, Houston, Texas	30,000
Reactive Metals, Inc., Ashtabula, Ohio	<u>37,000</u>
	189,000



For those four years, production and capacity utilization were as follows (in short tons):

	<u>Production</u>	<u>Capacity Utilization</u>
1969	164,700	87%
1970	171,200	91%
1971	153,100	81%
1972	159,900	85%

#### c. Captive Usage

Sodium is an overwhelmingly "captive" product for tetraalkyl lead and other uses. Production is in the hands of three companies—DuPont, Ethyl, and Reactive Metals. DuPont and Ethyl have 83% of the nation's tetraalkyl lead manufacturing capacity. Reactive Metals has been the predominant user of sodium for titanium reduction. The highly captive market indicates that decisions regarding sodium metal production will be made in direct consequence of the manufacturers' experience with the sale of end products, primarily tetraalkyl leads.

#### d. Demand Growth

Automobile emission controls will severely decrease the total amount of lead used in gasoline. Likewise, a general decline in aerospace, commercial, and military aircraft and missile spending is causing a dramatic drop in the demand for titanium. Demand for sodium metal may decrease by almost one-third by 1976 or 1977.

#### e. Price Elasticity of Demand

Because the cost of pollution abatement for producing sodium metal is only a very small fraction of the market price for tetraalkyl lead, increased abatement costs will not cause the integrated tetraalkyl lead manufacturers to cut back sodium production or close plants. However, decreased market demand for the lead may result in cutbacks and may make it difficult to pass sodium abatement costs on to the purchasers of the lead.

#### f. Basis for Competition

Most sodium production is captive. Other sales, however, are made primarily on the basis of price. The list price during 1970-1972 has been 18-3/4¢/lb., tanks, works.

#### g. Market Share Distribution

Sodium production and tetraalkyl lead production are concentrated among only a few large companies, all of which have sizable production and comparably sized plants. This condition is favorable for passing on cost increases to consumers.

### 3. Plant Shutdown Impact

The after-tax pollution abatement costs to reach B.P.T. and B.A.T. levels are provided by the Development Document at approximately \$5.00 per ton of sodium produced. We estimate sodium manufacturing costs at \$200 per ton including a \$60 per ton credit for chlorine produced as a by-product from the electrolysis of sodium chloride. The list price for sodium metal is \$375 per ton but we estimate the average price of product sold or transferred is \$220 per ton. Effluent control costs to achieve B.P.T. and B.A.T. levels would therefore account for approximately 25% of total profitability. The achievement of E.P.P. levels would require costs of approximately 10% of estimated profitability.

The abatement costs are less significant when one compares them to the list price of tetraethyl lead, the largest selling type of tetraalkyl lead. The tetraethyl lead list price is \$750 per ton. Only .325 pounds of sodium metal is used to make one pound of tetraethyl lead. The sodium after-tax abatement cost of about \$1.00 per ton of tetraethyl lead is quite small compared to the lead's price and probable profitability.

#### a. Cash Flow

The magnitude of the abatement costs are too small to seriously affect cash flow even if adverse tetraalkyl lead market conditions make it difficult to pass the abatement costs on to the consumer.

#### b. Ratio of Investment in Treatment Facilities to Net Fixed Investment

A 25,000 tons capacity sodium plant requires a fixed investment of approximately \$15 million or about \$600 per ton of capacity. For that sized plant the investment for pollution abatement at B.P.T. and B.A.T. levels is about \$700,000. This ratio of abatement investment (5%) is, therefore, probably not initially restrictive.

#### c. Integration

Since the manufacturing of sodium metal is overwhelmingly controlled captively by the manufacturers of tetraalkyl leads, they would be reluctant to close sodium plants unless they were cutting back on alkyl lead production for other reasons.

#### d. Emotional Commitment

DuPont, because of its diversity, is probably not deeply committed to sodium metal or tetraalkyl lead production. However, for Ethyl Corp. tetraalkyl leads are an important part of their business in the United States and abroad, so they would probably have significantly greater interest in continued production.

## F. SODIUM SULFITE

### 1. Summary

The EPA Development Document provides water effluent treatment costs which are unlikely to have any significant economic impact on the small volume of merchant sodium sulfite produced by the process considered in that Development Document. For the uses to which we believe such special grades of sodium sulfate are marketed, the additional cost of water effluent treatment can be either absorbed or compensated for by appropriate price increases.

Our analysis of economic impact is predicated on the structure of water effluent treatment costs described in the Development Document. Due to different approaches to reach different levels and the consequent recovery of different by-product chemicals, costs per ton of product produced decrease dramatically between exemplary plant levels and best available treatment levels. Effluent control costs to reach exemplary plant practice levels are specified at approximately \$3.00 a ton in producing sodium sulfite through the reaction of sulfur dioxide with soda ash. To achieve B.P.T. levels requires approximately 10¢ per ton less, and to reach B.A.T. levels provides a net income of approximately \$1.55 per ton due to the recovery of sodium sulfite. The Development Document does not specify why, given this possibility, the industry does not currently utilize the recovery system proposed.

The economic impact analysis is difficult due to the fact that the great bulk of merchant sodium sulfite produced and sold is by-product from the production of phenol and resorcinol. A relatively small proportion, probably less than 20%, is high purity material manufactured from soda ash for photographic use and sold at what we believe to be a substantially higher price.

### 2. Price Impact

As indicated in the impact analysis matrix, the price increase constraints relative to sodium sulfite water treatment costs are the following.

#### a. Ratio of Before Tax Treatment Cost to Selling Price

The impact analysis matrix shows values ranging from 6% for E.P.P. and B.P.T. to minus 3% for B.A.T. effluent control practices. These treatment costs consider only the process for the manufacture of sodium sulfite from sulfur dioxide and soda ash. The values given are based on the average prices for sodium sulfite obtained from the Census Bureau data for 1971. We believe the relatively small proportion of the sodium sulfite produced by this process, however, sells at significantly higher prices than the average price. Photographic grade sodium sulfite sells at a price of around \$200 per ton. On the assumption that sodium sulfite manufactured by the process described goes

principally for photographic applications, the ratio of before tax treatment cost to selling price for this particular product is approximately one-quarter of the ratios shown in the impact analysis matrix.

#### b. Substitute Products

Three fourths or more of the sodium sulfite produced in the United States is used for the production of neutral sulfite semichemical pulp. The pollution, air pollution and particularly water pollution, aspects of the NSSC process can be significantly relieved by the use of new processes which produce a pulp of similar properties without the use of sodium sulfite whether purchased or produced in situ. Thus the largest market for sodium sulfite, one which consumes a majority of the sodium sulfite produced, can utilize substitute products for sodium sulfite if there were significant price increases based on water effluent treatment. Even more important, however, is the probability that such substitution will be effected regardless of whether there are price increases for sodium sulfite. The paper pulp industry will find it more and more difficult to produce and use captive sodium sulfite because of the restricted availability of soda ash as a raw material and the water effluent problems attendant to the manufacture and use of sodium sulfite in the pulping process.

#### c. Demand Growth

Demand for sodium sulfite has increased in this past decade at a rate of around 4% per year. If, as is indicated, there is major substitution of sodium sulfite used in the production of NSSC type pulp by new non-sulfur utilizing processes, there will be reduced total consumption of sodium sulfite. Even those pulp mills remaining on the use of neutral sulfite semichemical pulping will tend to have a higher future recovery of sulfur and sodium values from pulp liquor due to more stringent effluent controls on the pulp and paper industry. This will mean, therefore, less sodium and sulfur values required for make-up per ton of pulp produced.

#### d. Abatement Cost Differences

There are quite probably differences in pollution abatement costs between various producing plants. The largest differences very probably would be between those plants producing by-product sodium sulfite from phenol or resorcinol processes and the producers of sodium sulfite by reaction of soda ash and sulfur dioxide. The latter category, the process covered by the Development Document, includes plants with capacities which vary by more than threefold. We would expect there would be significant differences in effluent control costs between the smallest and largest of these plants. The plant specified in the Development Document is for approximately 16,000 tons per year capacity, a relatively large sodium sulfite plant utilizing soda ash and sulfur dioxide.



#### e. Basis for Competition

For the major market for sodium sulfite, the production of NSSC pulp, price has been the primary consideration in determining source of supply, including the decision to make or buy. In the future, however, the make or buy decision will be complicated by the impact of (1) periods of poor availability of soda ash resulting from shutdowns of Solvay process operations; (2) water pollution problems at NSSC plants leading to installation of direct sodium sulfite recovery; and (3) availability of non-sulfur processes for manufacture of pulp similar in properties to NSSC pulp. The basis of competition for high purity sodium sulfite has been marketing capability as well as price.

#### 3. Plant Shutdown Impact

The following factors relate to the sodium sulfite plant shutdown decision.

##### a. Ratio of After-Tax Treatment Cost to After Tax Net Income

As previously described, the only treatment cost available from the Development Document is based on soda ash and sulfur dioxide process. We have not developed detailed economics of manufacture by this process as this was not included in the scope of our assignment. We estimate that treatment costs for all three levels of treatment described in the impact matrix would be low relative to profitability. This is based on the assumption that the major part of the product produced is being sold at \$200 a ton to the photographic chemical market.

Regardless of profitability, the effluent treatment described by the Development Document to achieve B.A.T. levels would be low relative to profitability as the Development Document specifies that by-product recovery results in the development of a negative cost of about \$1.55 per ton of product produced.

The consideration of this ratio is not valid for the great majority of merchant sodium sulfite produced as by-product of phenol and resorcinol production. No costs are available from the Development Document relative to effluent control and a description of profitability of sodium sulfite production via these by-product routes is necessarily arbitrary as the product must be produced, although not necessarily recovered, as a consequence of the production of the major product of concern.

##### b. Other Environmental Problems

Because sulfur compounds tend to create both air and water pollution problems, and because the production of sodium sulfite is generally associated with phenol production (by-product thereof), resorcinol production (by-product thereof) or pulp production (captive raw material utilization), it is difficult to conceive of such operations having an isolated problem of water pollution tied to the sodium sulfite production alone.

#### c. Emotional Commitment

Neither the by-product operations nor the NSSC pulp captive production represents emotional commitment. These are essentially viewed as economic necessities.

#### d. Ownership

Except for the captive NSSC production, sodium sulfite capacity is owned by large multi-product chemical companies with other opportunities for investment besides that represented by sodium sulfite manufacture.

### G. CALCIUM CHLORIDE

#### 1. Summary

Because the water effluent treatment costs provided by the Development Document are less than 1% of sales price, we do not foresee significant economic impact for plants where such costs are applicable. High capacity utilization and concentration of production within two major chemical companies are factors which provide an environment in which the costs incurred may be compensated for by price increases.

#### 2. Price Impact

As indicated in the impact analysis matrix, the price increase constraints relative to calcium chloride water effluent treatment costs are the following:

##### a. Captive Usage

Captive usage is low in the sense that most of the calcium chloride produced is sold as calcium chloride by the producer and the opportunities for forward integration into products for which calcium chloride is a raw material are limited. Over half of the calcium chloride produced is marketed for highway deicing or rural road dust control, markets served by the calcium chloride producers.

##### b. Demand Growth

The demand growth over the past five years has been limited to 3-4% per year and this is unlikely to change dramatically in the future. The highway deicing market loss due to local legislation restricting the consumption of salt mixtures (rock salt and calcium chloride) are compensated for by growth in other markets.

Furthermore, the relatively low demand growth is compensated for by the high capacity utilization factor of 90%. High capacity



utilization has resulted from plant shutdowns attributed to unfavorable economics and concern about the future markets. The market concerns are ecologically directed and primarily focused on use of calcium chloride and rock salt for highway ice control. The ice-control market has declined from about one-third of the U.S. calcium chloride market to about one-quarter thereof. The plants that were shut down derived by-product calcium chloride from soda ash production by the Solvay process. Reduction of total capacity from these shutdowns in the past few years amounted to about 25% with half of this reduction now regained through expansion of by-product calcium chloride recovery from brine chemical operations for which magnesium hydroxide is the product of primary interest. Capacity utilization is appropriate for the demand growth and therefore low demand growth is not per se a price increase constraint for calcium chloride.

#### c. Basis for Competition

Historically the price competition for the highway and rural road markets for calcium chloride has been stringent, with freight equalization limiting the marketers' geographic scope. Thus a significant price increase for the product from a specific plant would provide an umbrella for a competitive plant to broaden its geographic scope. The fact that price has been the primary basis for competition is a valid price increase constraint. This is now compensated for by the heavy concentration of market share distribution by two major suppliers holding 80% or more of the market.

#### d. Number of Producers

While there are about ten U.S. producers of calcium chloride, only two are large volume producers. Five of the smaller volume plants are located in the far western states of California, Washington, and Utah and limited by freight equalization to the western U.S. market. Thus the number of producers is not an effective price increase constraint.

The above constraints are unlikely to be significant because they are largely compensated for by high capacity utilization and concentration of production. Furthermore the water effluent treatment costs provided by the Development Document are only 0.5% of the sales price. However, it is important to emphasize that the effluent treatment costs are not applicable to the production of calcium chloride as a by-product from the manufacture of soda ash by the Solvay process. Furthermore, such calcium chloride treatment costs are associated with soda ash effluent treatment costs. This distinction is important in examining the following factors relevant to a plant shutdown decision.

### 3. Plant Shutdown Impact

#### a. Ratio of Treatment Cost to Net Income

As calcium chloride is a by-product of other operations, the definition of net income due to its sale is necessarily arbitrary. In

view of the very low treatment cost provided by the Development Document--18 cents before taxes per ton of product--we have assumed this to be a low proportion of the net income assigned to the sale of calcium chloride.

#### b. Ownership

At least 90% of the calcium chloride capacity is owned by large multi-industry companies, so the plant shutdown decision is unhampered since it is not the major business of the producer. This is evidenced by shutdowns of two calcium chloride operations in the United States in recent years. Thus, if there are price increase constraints, further plant shutdowns might be expected. It is our evaluation, however, that price increase constraints will not prevent necessary increases to cover those water effluent treatment costs presented in the Development Document. Nevertheless, these same water effluent costs do not apply to production of calcium chloride as a by-product of soda ash which is a significant portion of the existing calcium chloride capacity. That capacity which is dependent upon continuance of soda ash production relates primarily to soda ash water effluent treatment costs also presented in this document.

### H. SYNTHETIC SODA ASH

#### 1. Summary

As estimated by the Development Document, incremental water treatment costs for synthetic soda ash producers to achieve B.P.T. and B.A.T. levels are 0 and \$0.66 per ton, respectively. The B.A.T. cost constitutes 1.9% of the \$34.60 per ton selling price in 1972. Even this nominal cost, however, could not be passed on as a price increase by the synthetic soda ash producers if producers of natural soda ash, the primary competitive product to synthetic soda ash, did not correspondingly raise prices. On the other hand, in spite of narrow profit margins for synthetic soda ash producers, the modest magnitude of the after-tax treatment cost which would have to be absorbed and the small amount of plant investment for treatment facilities in comparison to existing fixed investment in production facilities are insufficient to cause plant shutdowns.

#### 2. Price Impact

Competitive conditions in the synthetic soda ash industry are such that severe constraints exist which would make specific price increases to cover large, new costs for water treatment extremely difficult. The primary price increase constraints are the existence of substitute products, declining production of synthetic soda ash, unequal abatement cost differences (with respect to natural soda ash), high price elasticity of demand, and an undifferentiated product wherein price is the only basis for competition.

These constraints against price increase outweigh those factors in the industry which, in the absence of constraints, might make it possible to increase prices. These include a relatively high operating rate at the present time (approximately 95% of capacity in 1972), captive usage representing very nearly 25% of production, the almost complete absence of foreign competition, concentrated market share distribution, and the relatively few (five) producers.

No price increases would be necessary for B.P.T. since the guidelines recommendation is for no change in treatment from current industry practice. That is, the incremental costs for B.P.T. will be zero. (In fact, the Development Document indicated that the E.P.P. resulted in a profit of \$1.17 per ton of soda ash produced. The profit resulted from converting 20% of the effluent to saleable calcium chloride.) The revised cost for B.A.T. was estimated at \$0.66 per ton, equivalent to 1.90% of the 1972 selling price of \$34.60 per ton. Even this nominal charge could not be passed on as price increases by the Solvay soda ash producers if at the time the standard comes into effect there are ample supplies of natural soda ash and caustic soda.

#### a. Substitute Products

Synthetic soda ash competes directly with natural soda ash as well as caustic soda and, to a lesser extent, with other alkaline materials such as lime and salt cake. The major competition to synthetic soda ash comes from natural soda ash. Natural soda ash is produced primarily in Green River, Wyoming, and to a lesser degree, from naturally occurring salt lake brines in California. Preliminary Commerce Department data indicate that in 1973, production of natural soda ash (estimated at approximately 4 million tons) will surpass production of synthetic soda ash (estimated at 3.6 million tons) for the first time. As recently as 1960, synthetic soda ash represented 85% of total U.S. production of soda ash. There is no significant quality or performance difference between natural and synthetic ash. The loss of market to natural soda ash has been due to significantly lower costs of manufacture for the natural product.

In addition to natural soda ash, synthetic soda ash also competes with caustic soda (which can be substituted in most of the soda ash applications). The substitution of caustic soda for soda ash has occurred at varying rates for the past 15 years or so. For example, soda ash has lost all of the alumina, a major part of the paper, and some phosphate and silicate markets to caustic soda. The selection of soda ash or caustic soda is almost entirely a matter of economics, viz. the delivered price of the two materials on an  $\text{Na}_2\text{O}$  equivalent basis. At the present time both soda ash and caustic soda are in tight supply so that the erosion of soda ash markets by caustic soda has been temporarily arrested.

To a lesser extent soda ash competes with lime and salt cake (sodium sulfate), both lower cost materials than soda ash but with less desirable properties for most of the soda ash applications.

#### b. Demand Growth

Although overall demand for U.S. soda ash (domestic market plus exports) has grown at an average annual compound rate of about 3% in the last ten years, the output of synthetic soda ash has actually declined. For example, in the mid-1960's synthetic soda ash production was approximately 5 million tons versus 4.3 million tons in 1972. As mentioned, 1973 production will apparently total 3.6 million tons. All of the growth in the total soda ash market has been supplied by natural soda ash (which has also made up the shortfall in soda ash supply resulting from the decline in synthetic soda ash production).

#### c. Abatement Cost Differences

There is no information in the Development Document which would infer that there are abatement cost differences among the synthetic soda ash producers themselves. However, because the producers of natural soda ash are not faced with comparable water treatment costs, and because synthetic soda ash is directly competitive with natural soda ash, a condition of unequal abatement costs exists which would make it difficult for the synthetic soda ash producer to increase prices if producers of natural soda ash (or caustic soda) did not want to raise prices.

#### d. Price Elasticity of Demand

Because synthetic soda ash and natural soda ash are completely substitutable one for the other, the price of either one could not be raised to a premium versus the other without a shift in market demand to the lower cost form. A similar situation exists with respect to caustic soda, i.e., if synthetic soda ash prices were increased such that caustic soda became less costly on an ash equivalent delivered basis, there would be a shift of market demand away from synthetic soda ash as sodium alkali consumers used increasing amounts of caustic soda. Because the demand for synthetic soda ash (in competition with natural soda ash or caustic soda) is very sensitive to its price, it would be difficult for the synthetic soda ash producers to raise prices to cover increased costs of water treatment.

#### e. Basis for Competition

Price is the basis for competition among soda ash producers, representing another strong constraint against higher prices for one of the competing forms of sodium alkali.

#### 3. Plant Shutdown Impact

The synthetic soda ash industry has been characterized in recent years by long periods of marginal profitability interspersed with shorter periods of improved profitability (as in late 1973) when competitive conditions in the industry allowed producers to raise prices in concert with higher natural soda ash and caustic soda prices. The long-term outlook is for minimal and diminishing profit margins for synthetic soda



ash producers. In spite of these conditions, the B.A.T. costs of \$0.33 per ton (after taxes) are not sufficient by themselves to cause plant shutdowns. (As indicated B.P.T. costs will be zero for the industry.)

#### a. Ratio Treatment Costs to Net Income

Average after-tax profits for synthetic soda ash producers in 1972 are estimated at \$0.75 per ton. In comparison, the B.A.T. after-tax cost of \$0.33 per ton would represent very nearly 44% of profits.

#### b. Cash Flow

In 1972 cash flow for the typical synthetic soda ash plant was \$1.75 per ton, made up of the aforementioned \$0.75 per ton of after-tax profits plus \$1.00 per ton of depreciation. Even after the B.A.T. costs of \$0.33 per ton, therefore, cash flow would remain positive.

#### c. Treatment Facilities Investment

The typical soda ash plant in 1972 had a fixed investment of \$8.75 million. The incremental investment for B.A.T. of \$1.20 million therefore represents 13.7% of existing plant investment. The investment required for B.A.T. is not a significant sum for the major chemical companies comprising the list of synthetic soda ash producers, either in absolute terms or in comparison with existing fixed plant investment.

#### d. Integration

The soda ash industry uses some of its output (approximately 25%) captively for production of sodium phosphates, sodium silicates, sodium bicarbonate, sodium chromate, glass (to a very minor extent) and alkaline cleaners. Some of the producers of synthetic soda ash are integrated backward to a minor extent, primarily to lime or limestone. In any event, the degree of vertical integration for any single producer is not sufficient justification for continued plant operation if the economics are unsatisfactory.

### I. POTASSIUM SULFATE

#### 1. Summary

The largest quantity of potassium sulfate produced in the U.S. derives from the separation of natural brines. The second most significant process is the manufacture of potassium sulfate from langbeinite through the reaction of this ore with potassium chloride to produce potassium sulfate with magnesium chloride as by-product. Langbeinite processing accounts for approximately 40% of potassium sulfate capacity in the United States. Small amounts are derived from the Hargreaves Process and Mannheim Process in which potassium chloride is treated with sulfur dioxide and sulfuric acid respectively.

The guideline contractor provided treatment costs for the langbeinite process only. On the basis of these given costs, our calculations of profitability, and our estimates of the producers capability of raising prices, we do not expect any significant economic impact on the producers of potassium sulfate by the langbeinite process in meeting the standards established by the Development Document for exemplary plant, best practicable technology or best available technology treatment levels. Producers will raise prices and/or absorb costs without shutting down their facilities.

The Development Document specifies a total annual cost of \$395,000 for effluent treatment for a potassium sulfate plant of 500 tons per day capacity. Total annual cost including energy and power costs are \$166,000. The Development Document was prepared significantly in advance of the energy shortage and rising energy prices manifest late in 1973. Therefore, we believe that it does not accurately reflect the future costs of effluent treatment. Obviously, the document would also not reflect the capability of the langbeinite plant operators to obtain the necessary energy for effluent treatment.

#### 2. Price Impact

As shown in our impact analysis matrix, there are a number of factors mitigating against price increases by the industry. In spite of these, which are explained in detail below, we believe that the industry will be able to pass on at least a portion of the additional pollution abatement costs incurred for effluent treatment. This belief is based on our expectation that capacity utilization is actually significantly higher than shown by examination of nominal capacity and that the two producers of potassium sulfate from langbeinite, together with the operators of the Great Salt Lake capacity, constitute a sufficiently concentrated production so as to be able to act in their own self interest and pass along additional costs incurred for pollution control.

This pricing flexibility is based on the assumption that  
(a) there will not be major new U.S. sources of potassium sulfate, and  
(b) export demand which constitutes a significant proportion of the total will not appreciably soften in future years.

#### a. Substitute Products

Potassium sulfate, potassium chloride, potassium magnesium sulfate, and potassium nitrate are utilized to provide potassium content for fertilizer application. Demand for potassium chloride, the lowest cost form of potassium, is far higher than for the other potassium salts. Potassium nitrate is very little used and potassium sulfate and potassium magnesium sulfate find application where farmers do not want the chloride ion provided with the use of potassium chloride. Potassium magnesium sulfate, obtained from refined langbeinites has a significantly lower potassium content than potassium sulfate but also has the additional virtue of contributing magnesium to those soils and for those crops where this is desirable.



There is some degree of flexibility of product substitution in the sense that if potassium sulfate prices change dramatically relative to the other sources of potassium, then at least some portion of the consumers of potassium sulfate would probably convert to other forms. We consider it quite unlikely, however, that the relative prices of the materials will change dramatically so as to significantly distort existing patterns of consumption.

#### b. Capacity Utilization

The U.S. Department of Commerce current industrial reports provide potassium sulfate shipments and production. On 100% potassium sulfate basis, 1971 production was 450,000 tons and 1972 production 402,000 tons. Nominal capacity was as follows:

#### POTASSIUM SULFATE NOMINAL CAPACITIES (Thousands of Tons/Year)

		100% K <sub>2</sub> SO <sub>4</sub>
American Potash & Chemical (Kerr McGee)	Trona, California	65
Duval Corp. (Pennzoil United)	Carlsbad, N. Mexico*	65
IMC	Carlsbad, N. Mexico*	65
Potash Corp. of America (Ideal Basic Industries)	Dumas, Texas** Fort Worth, Texas***	22 22
Southwest Potash (AMAX)	Vicksburg, Mississippi	
Others (by-product)	Colorado, Texas, Ohio	20
Great Salt Lake Minerals & Chemicals (Gulf Resources & Chemical Corp.--51% and Salzdefurth A.G.--49%)	Great Salt Lake, Utah	185 527

\*From langbeinite.

\*\*Hargreaves process.

\*\*\*Mannheim process.

On the basis of the capacity shown, production during 1972 was at 76% of the total available capacity. Capacity in fact is highly variable. Both Duval and IMC have probably switched some portion of their available capacity to the manufacture of potassium magnesium sulfate. In addition, Great Salt Lake Minerals & Chemicals has a varying capacity depending upon operating and weather conditions. This company's production of potassium sulfate comes from separation of the salt from brines concentrated in ponds by solar evaporation.

At the present time, there does not seem to be significant surplus capacity overhanging the market. Prices of the product are relatively firm and the market is not behaving as though competitive producers were attempting to utilize over-capacity by bidding for available business.

Two additional potential producers are Occidental Petroleum which is considering production from brines at Searles Lake and a venture by National Lead which has been attempting to develop a brine separation facility at the Great Salt Lake in Utah. The National Lead venture initially planned production of 100,000 tons per year of potassium sulfate. If the capacity for potassium sulfate extraction should be substantially increased by one or both of these producers entering the business, capacity utilization would decline significantly and inhibit opportunity for future price increases.

#### c. Captive Usage

All of the producers listed above distribute potassium sulfate through fertilizer distributors. IMC may also undertake direct sale to farmers. We do not believe, however, that this is a significant restraint in terms of the pricing capability of the producers.

#### d. Demand Growth

Shipments of potassium sulfate by U.S. producers over the past five years were as follows:

1968	321,000 tons
1969	263,000
1970	86,000
1971	483,000
1972	388,000

Over this period of time, domestic demand has apparently declined while exports have significantly increased. In the 1967-1968 fertilizer season, exports totaled 104,000 tons on a 100% K<sub>2</sub>SO<sub>4</sub> basis, while imports were 61,000 tons, resulting in a net export balance of 43,000 tons. 1972 exports totaled 208,000 tons, excluding Canada, and imports totaled 59,000 tons. Thus while U.S. shipments of potassium sulfate

increased between 1968 and 1972 by about 76,000 tons, this was more than accounted for by the increase in net exports over the period of time.

Industry trade estimates suggest an increasing export market at a growth rate of better than 5% per year for the next several years. Domestic demand is expected to demonstrate little or no growth.

#### e. Abatement Cost Differences

There are both manufacturing cost differences and abatement cost differences among the various producers. The Hargreaves and Mannheim processes are significantly higher cost than the langbeinite process, and, we presume, they have a higher cost than the separation of brines. In the latter case, manufacturing costs will necessarily be somewhat arbitrarily defined because of the variety of co-products from any particular brine.

Abatement costs are provided by the Development Document only for a plant operating on the langbeinite process of 500 tons per day. We assume a smaller plant such as operated by Duval Corporation would have a significantly higher unit cost for pollution abatement. The separation of brine, would, we assume, have no pollution abatement costs associated with the activity, as the process is essentially the extraction of soluble salts from a natural brine.

#### f. Price

Producers compete on prices more than any other basis and this does impose some restraint on increasing prices. In this case, however, we believe that this effect is outweighed by other conditions involving relatively high fertilizer demand compared to active capacity and that the basis of competition will not be sufficient to restrain the recovery of additional costs through price increases.

### 3. Plant Shutdown Impact

The Development Document specifies only one type of treatment for effluent control to meet all technology control levels. This provides for an increase from simply pond settling of muds to evaporation and recovery of liquor chemicals and water. By our estimates, the cost of evaporation even at energy values previously assumed, constitutes approximately 16% of profits. These estimates are based on a price of \$45.90 per ton of  $K_2SO_4$  and a manufacturing cost of \$35.00 per ton to yield a profit before taxes of around \$15.00 per ton. The increase in abatement cost suggested by the Development Document totaled \$2.37 per ton assuming 320 operating days per year. Thus while the abatement costs are significant, the profitability of the operation would appear high enough to make these tolerable even without compensating price increases.

It seems to us that the real issue facing the producers of potassium sulfate via the langbeinite process is that they will have to make the required investment in the face of additional potential competition from producers of potassium sulfate from natural brines. This additional investment, described in the Development Document, would total \$660,000 for a plant producing 500 tons per day of potassium sulfate. By our calculations, a plant this size operating at 80% of capacity and selling at current prices should be able to pay out this investment in less than one year. On the basis of these calculations, we believe the producers of potassium sulfate by the langbeinite process will not close their plants, although marketing conditions permitting, it may be more advantageous for them to shift a greater proportion of their capacity to the sale of refined langbeinite as sulfate of potash magnesium.

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*Development Document for Effluent Limitations Guidelines  
and New Source Performance Standards for the*

# MAJOR INORGANIC PRODUCTS

*Segment of the*

*Inorganic Chemicals Manufacturing*

*Point Source Category*

MARCH 1974



U.S. ENVIRONMENTAL PROTECTION AGENCY

Washington, D.C. 20460



DEVELOPMENT DOCUMENT  
for  
EFFLUENT LIMITATIONS GUIDELINES  
and  
NEW SOURCE PERFORMANCE STANDARDS  
for the  
MAJOR INORGANIC PRODUCTS SEGMENT OF THE  
INORGANIC CHEMICALS MANUFACTURING  
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5072

# ABSTRACT

This document presents the findings of an extensive study of major inorganic chemicals manufacture for the purpose of developing effluent limitation guidelines for existing point sources and standards of performance and pretreatment standards for new sources to implement Sections 304, 306 and 307 of the Federal Water Pollution Control Act, as amended (33 U.S.C. 1551, 1314, and 1316, 86 Stat. 816 et. seq.) (the "Act").

Effluent limitations guidelines contained herein set forth the degree of effluent reduction attainable through the application of the best practicable control technology currently available and the degree of effluent reduction attainable through the application of the best available technology economically achievable which must be achieved by existing point sources by July 1, 1977 and July 1, 1983, respectively. The standards of performance and pretreatment standards for new sources contained herein set forth the degree of effluent reduction which is achievable through the application of the best available demonstrated control technology, processes, operating methods, or other alternatives.

Based on the application of best practicable technology currently available 12 of the 22 chemicals under study can be manufactured with no discharge of process waste water pollutants to navigable waters. With the best available technology economically achievable 20 chemicals can be manufactured with no discharge of process waste water pollutants to navigable waters. No discharge of process waste water pollutants to navigable waters is required as a new source performance standard for all chemicals except titanium dioxide, chlorine, sodium dichromate, sodium sulfite and sodium chloride.

Supporting data and rationale for development of the effluent limitations guidelines and standards of performance are contained in this report.

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SECTION I

CONCLUSIONS

For the purpose of establishing effluent limitation guidelines and standards of performance, the major inorganic products segment of the inorganic chemicals manufacturing point source category was divided into 22 product subcategories consistent with the chemical produced. In some cases, the product subcategory was further subdivided to reflect different manufacturing processes used to produce the same chemical. This method of categorization reflects differences in the nature of raw wastes generated in the manufacture of different chemicals, as well as its treatability. Factors such as plant age, plant size and geographical location did not justify further segmentation of the industry.

Based on best practicable control technology currently available (EPCTCA), 12 of the 22 chemicals under study can be manufactured with no discharge of process waste water pollutants to navigable waters. With the application of best available technology economically achievable (BATEA), 20 of the 22 chemicals can be manufactured with no discharge of process waste water pollutants to navigable waters. No discharge of process waste water pollutants to navigable waters is, also, achievable as a new source performance standard (NSPS) based on the best demonstrated control technologies, processes, operating methods or other alternatives (BDCT) for all chemicals except titanium dioxide, chlorine, sodium dichromate, sodium sulfite, and sodium chloride.

This study included 22 of the major inorganic chemicals of SIC categories 2812, 2816, and 2819 which discharge significant quantities of process waste water pollutants into the navigable waters of the United States. A forthcoming study includes certain other inorganic chemicals and industrial gases whose annual U.S. production volume exceeds 450 kkg (500 ton) with significant waste discharge potential.



## SECTION II

### RECOMMENDATIONS

The effluent limitation guidelines representing the effluent reduction attainable by the application of best practicable control technology currently available and the effluent reduction attainable by the application of best available technology economically achievable are shown in Table 1. Also shown are the new source performance standards for each chemical subcategory.

The figures in the table represent the thirty-day average allowable discharge. In all cases the daily maximum is twice the thirty-day average. All process waste water discharges must be within the pH range of 6.0 - 9.0. Effluent limitation guidelines for non-contact cooling water and waste streams resulting from steam and water supply are being developed in a separate study.

The technologies on which such guidelines are based are discussed in detail in Sections III - XI, along with the rationale for selecting the various levels of technology.

Table 1. EFFLUENT LIMITATION OUTLINES  
AND NEW SOURCE PERFORMANCE STANDARDS

Product Subcategory	Limitation based on BPTCA (kg/kg)	Limitation based on LATA (kg/kg)	New Source Performance Standard (kg/kg)
Aluminum Chloride	no discharge of pump*	no discharge of pump	no discharge of pump
Aluminum Sulfate	no discharge of pump	no discharge of pump	no discharge of pump
Calcium Carbide	no discharge of pump	no discharge of pump	no discharge of pump
Calcium Chloride	TSS 0.0002	no discharge of pump	no discharge of pump
Calcium Oxide and Hydroxide Chloride	no discharge of pump	no discharge of pump	no discharge of pump
a) mercury cell process	TSS 0.32	no discharge of pump	TSS 0.22
b) diaphragm cell process	Mercury 0.00014	no discharge of pump	Mercury 0.00007
	TSS 0.32	no discharge of pump	TSS 0.22
Hydrochloric Acid	Lead 0.0025	no discharge of pump	Lead detectable limit
Hydrofluoric Acid	no discharge of pump	no discharge of pump	no discharge of pump
Hydrogen Peroxide	no discharge of pump	no discharge of pump	no discharge of pump
a) organic process	TSS 0.4	no discharge of pump	no discharge of pump
b) electrolytic process	TSS 0.22	no discharge of pump	no discharge of pump
	TSS 0.0025	no discharge of pump	no discharge of pump
	Cyanide 0.0002	no discharge of pump	no discharge of pump
Hydrochloric Acid	no discharge of pump*	no discharge of pump	no discharge of pump
Potassium Metal	no discharge of pump	no discharge of pump	no discharge of pump
Potassium Dichromate	no discharge of pump	no discharge of pump	no discharge of pump
Potassium Sulfate	no discharge of pump	no discharge of pump	no discharge of pump
Sodium Bicarbonate	no discharge of pump	no discharge of pump	no discharge of pump
Sodium Carbonate	no discharge of pump	no discharge of pump	no discharge of pump
Sodium Chloride	TSS 0.27	TSS 0.10	no discharge of pump
a) solar evaporation process	uncontaminated waste bitterns may be returned to the source	same as BPTCA	same as BPTCA
b) solution brine-mining process	TSS 0.17	no discharge of pump	no discharge of pump
Sodium Dichromate	TSS 0.22	no discharge of pump	TSS 0.15
	Cr(VI) 0.0044	no discharge of pump	Cr(VI) 0.0044
	Cr(+6) 0.0005	no discharge of pump	Cr(+6) 0.0005
Sodium Metal	TSS 0.23	no discharge of pump	no discharge of pump
Sodium Silicate	TSS 0.009	no discharge of pump	no discharge of pump
Sodium Sulfite	TSS 0.016	no discharge of pump	no discharge of pump
	COD 1.7	no discharge of pump	TSS 0.016
Sulfuric Acid	(as Cr <sub>2</sub> O <sub>3</sub> )	no discharge of pump	COD 1.7
Titanium Dioxide	no discharge of pump	no discharge of pump	(as Cr <sub>2</sub> O <sub>3</sub> )
a) chloride process	TSS 2.3	TSS 1.3	no discharge of pump
b) sulfate process	Iron 0.36	Iron 0.18	TSS 1.3
*process waste water pollutants	TSS 10.5	TSS 5.3	Iron 0.16
	Iron 0.84	Iron 0.42	TSS 5.3
			Iron 0.42

### SECTION III

#### INTRODUCTION

##### PURPOSE AND AUTHORITY

The United States Environmental Protection Agency (EPA) is charged under the Federal Water Pollution Control Act Amendments of 1972 with establishing effluent limitations which must be achieved by point sources of discharge into the navigable water of the United States.

Section 301(b) of the Act requires the achievement, by not later than July 1, 1977, of effluent limitations for point sources, other than publicly owned treatment works, which are based on the application of the best practicable control technology currently available as defined by the Administrator pursuant to Section 304(b) of the Act. Section 301(b) also requires the achievement by not later than July 1, 1983, of effluent limitations for point sources, other than publicly owned treatment works, which are based on the application of the best available technology economically achievable which will result in reasonable further progress toward the national goal of eliminating the discharge of all pollutants, as determined in accordance with regulations issued by the Administrator pursuant to Section 304(b) of the Act. Section 306 of the Act requires the achievement by new sources of a Federal standard of performance providing for the control of the discharge of pollutants which reflects the greatest degree of effluent reduction which the Administrator determines to be achievable through the application of the best available demonstrated control technology, processes, operating methods, or other alternatives, including, where practicable, a standard permitting no discharge of pollutants. Section 304(b) of the Act requires the Administrator to publish within one year of enactment of the Act, regulations providing guidelines for effluent limitations setting forth the degree of effluent reduction attainable through the application of the best practicable control technology currently available and the degree of effluent reduction attainable through the application of the best control measures and practices achievable including treatment techniques, process and procedure innovations, operation methods and other alternatives. The regulations proposed herein set forth effluent limitations guidelines pursuant to Section 304(b) of the Act for the inorganic chemicals manufacturing point source category.

Section 306 of the Act requires the Administrator, within one year after a category of sources is included in a list published pursuant to Section 306(b) (1) (A) of the Act, to propose regulations establishing Federal standards of performance for new sources within such categories. The Administrator published in the Federal Register of January 16, 1973 (38 F.R. 1624), a list

of 27 point source categories. Publication of the list constituted announcement of the Administrator's intention of establishing, under Section 306, standards of performance applicable to new sources within the inorganic chemicals manufacturing point source category, which was included within the list published January 16, 1973.

#### SUMMARY OF METHODS USED FOR DEVELOPMENT OF EFFLUENT LIMITATION GUIDELINES AND STANDARDS OF PERFORMANCE

The Environmental Protection Agency has determined that a rigorous approach including plant surveying and verification testing is necessary for the development of effluent standards for industrial sources. A systematic approach to develop the required guidelines and standards includes the following:

- (a) Categorization of the industry and determination of those industrial categories for which separate effluent limitations and standards need to be set;
- (b) Characterization of the waste loads resulting from discharges within industrial categories and subcategories;
- (c) Identification of the range of control and treatment technology within each industrial category and subcategory;
- (d) Identification of those plants employing the best practical technology currently available (exemplary plants); and
- (e) Generation of supporting verification data for the best practical technology including actual sampling of plant effluents by field teams.

The culmination of these activities is the development of the guidelines and standards based on the best practicable technology currently available.

This report describes the results obtained from application of the above approach to the inorganic chemicals industry. Thus, the survey and testing covered a wide range of processes, products, and types of wastes. Studies of a total of twenty-five chemicals listed below are summarized in this Document.

#### Selected Inorganic Chemicals

Aluminum Chloride	Potassium Sulfate
Aluminum Sulfate	Sodium Bicarbonate
Calcium Carbide	Sodium Carbonate (Soda Ash)
Calcium Chloride	Sodium Chloride
Chlorine	Sodium Dichromate
Hydrochloric Acid	Sodium Hydroxide
Hydrogen Peroxide	Sodium Metal

Hydrofluoric Acid	Sodium Silicate
Calcium Oxide and Calcium Hydroxide	Sodium Sulfate
Nitric Acid	Sodium Sulfite
Potassium Chromates	Sulfuric Acid
Potassium Hydroxide	Titanium Dioxide
Potassium Metal	

The effluent limitation guidelines for existing point sources and standards of performance for new facilities were developed in the following manner. The point source category was first categorized for the purpose of determining whether separate limitations and standards are appropriate for different segments within a point source category. Such subcategorization was based upon raw material used, product produced, manufacturing process employed, and other factors. The raw waste characteristics for each subcategory were then identified. This included an analysis of (1) the source and volume of water used in the process employed and the sources of waste and waste waters in the plant; and (2) the constituents of all waste waters which result in degradation of the receiving water. The constituents of waste waters which should be subject to effluent limitations guidelines and standards of performance were identified.

The full range of control and treatment technologies existing within each subcategory was identified. This included an identification of each control and treatment technology, including both inplant and end-of-process technologies, which are existent or capable of being designed for each subcategory. It also included an identification of the quantity of constituents (including thermal) and the characteristics of pollutants resulting from the application of each of the treatment and control technologies. The problems, limitations and reliability of each treatment and control technology were also identified. In addition, the non-water quality environmental impact, such as the effects of the application of such technologies upon other pollution problems, including air, solid waste, noise and radiation were also identified. The energy requirements of each of the control and treatment technologies were identified as well as the cost of the application of such technologies.

Cost information contained in this report was obtained directly from industry during exemplary plant visits, from engineering firms and equipment suppliers, and from the literature. The information obtained from the latter three sources has been used to develop general capital, operating and overall costs for each treatment and control method. Costs have been put on a consistent industrial calculation basis of ten year straight line depreciation, plus allowance for interest at six percent per year (pollution abatement tax free money) and inclusion of allowance for insurance and taxes for an overall fixed cost amortization of fifteen percent per year. This generalized cost data, plus the



specific information obtained from plant visits, was then used for cost effectiveness estimates in Section VIII and wherever else costs are mentioned in this Document.

The data for identification and analyses were derived from a number of sources. These sources included EPA research information, published literature, qualified technical consultation, on-site visits and interviews at numerous inorganic chemical plants throughout the U.S., interviews and meetings with various trade associations, and interviews and meetings with various regional offices of the EPA. All references used in developing the guidelines for effluent limitations and standards of performance for new sources reported herein are included in Section XIII.

#### Exemplary plant selection

Eleven corporate headquarters were initially consulted for assistance in preparing a list of potentially exemplary plants. Eighty plants were studied in depth by consultations and review of plant data. Of these, sixty plants were visited for additional screening and data collection. Twenty-eight plants were then visited and sampled by the contractor. This sampling included all of the chemical processes subject to effluent limitations guidelines. The following criteria were developed and used for the selection of exemplary plants.

##### (a) Discharge effluent quantities

Plants discharging small quantities of pollutants or no process waste water pollutants were preferred. This minimal discharge may be due to reuse of water, raw material recovery and recycling, or good water conservation. The significant parameter was minimal waste added to effluent streams per weight of product manufactured.

##### (b) Water management practices

Use of good management practices such as water reuse, planning and in-plant water segregation, and the proximity of cooling towers to operating units, where airborne contamination of water can occur, were considered.

##### (c) Land utilization

The efficiency of land use was considered.

##### (d) Air pollution and solid waste control

Exemplary plants must possess overall effective air and solid waste pollution control in addition to water pollution control technology. Care was taken to insure that all plants chosen have

minimal discharges into the environment and that exemplary sites are not those which are exchanging one form of pollution for another of the same or greater magnitude.

##### (e) Effluent treatment methods and their effectiveness

Plants selected generally have in use the best currently available treatment methods, operating controls, and operational reliability. Treatment methods considered included basic process modifications which significantly reduce effluent loads as well as conventional end-of-pipe treatment methods.

##### (f) Plant facilities

All plants chosen as exemplary had all the facilities normally associated with the production of the specific chemical(s) in question. These facilities, generally, were plants which have all their normal process steps carried out on-site.

##### (g) Plant management philosophy

Plants were preferred whose management insists upon effective equipment maintenance and good housekeeping practices. These qualities are best identified by a high operational factor and plant cleanliness.

##### (h) Diversity of processes

On the basis that all of the above criteria are met, consideration was given to installations having a multiplicity of manufacturing processes. However, for sampling purposes, the complex facilities chosen were those for which the wastes could be clearly traced through the various treatment steps.

##### (i) Product purity

For cases in which purity requirements play a major role in determining the amounts of wastes to be treated and the degree of water recycling possible, different product grades were considered for sub-categorization.

#### Sampling of Exemplary Plants

The details of how the exemplary plants were sampled and the analytical techniques employed are fully discussed in Section V.

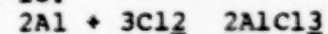
#### GENERAL DESCRIPTION OF THE INDUSTRY

Brief descriptions of each of the twenty-two chemical subcategories are presented below. Process flow sheets for the various subcategories are included. Production tonnages reported for 1971 were taken from Current Industrial Reports, Inorganic

Chemicals, U.S. Bureau of Census, Series M28A(71)-14.(1) These values are summarized in Table 2. Also included are production tonnages for years prior and subsequent to 1971, where available, and the number of plants producing each chemical.

#### Aluminum Chloride

The anhydrous product is produced by the reaction of gaseous chlorine with molten aluminum metal (scrap or scrap-pig mixture). The basic equation is:



Chlorine is introduced below the surface of the molten aluminum. The product sublimes and is collected by condensation. There are three types of products manufactured, all from the same general process:

- (1) Yellow - this product is made using a slight excess of chloride (0.0005 percent) and may contain some iron due to reaction of the chloride with the vessel;
- (2) White - this product has a stoichiometric aluminum and chlorine starting ratio; and
- (3) Grey - this product contains 0.01 percent excess aluminum. The unreacted aluminum raw waste load is higher for this grey material.

In most cases it makes little difference which of the above grades is employed. In some pigment and dye intermediate applications, the yellow material is preferred because it is free of elemental aluminum.

Aluminum chloride is also made from the reaction of bauxite, coke and chlorine. About 80 percent of all aluminum chloride made is anhydrous. A solution grade of aluminum chloride is also produced by reacting hydrated aluminum or bauxite ore with hydrochloric acid. A standard process diagram is shown in Figure 1.

Annual U.S. production in 1971 totalled 26,399 kkg (29,100 tons). The major use is as a catalyst in the petrochemical and synthetic polymer industries.

The 1971 production for the 28 percent solution product was 7,650 kkg (8,400 tons).

#### Aluminum Sulfate

Aluminum sulfate is produced by the reaction of bauxite ore, or other aluminum-containing compounds, with concentrated sulfuric acid (60°Be). The general equation of the reaction is:

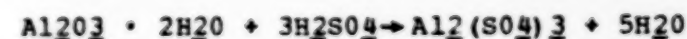


TABLE 2. U.S. Production of Inorganic Chemicals (Metric Tons)

	1973 (Est.)	1972	1971	1970	1969	No. of Plants (1971)
AlCl <sub>3</sub>		30,844	26,399	28,485	35,834	5
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>		1,019,670	1,084,080	1,080,451	1,136,696	100
CaCl <sub>2</sub>		447,240	566,988	717,579	776,546	7
CaCl <sub>2</sub>		861,821	1,100,409	1,006,000	1,066,843	9
Cl <sub>2</sub> (g)	9,480,031	8,952,052	8,483,947	8,857,700	7,801,748	63
HCl	2,131,873	1,996,703	1,904,171	1,827,060	1,733,621	83
HF		301,184	199,126	203,571	200,940	13
H <sub>2</sub> O <sub>2</sub>		68,039	58,060	55,338	58,967	5
Lime						
HNO <sub>3</sub>	6,731,276	6,369,311	6,116,208	6,059,055	5,422,060	97
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>		(Estimated) 4,309			5,844,960	72
KOH		161,478	179,622	158,756	160,570	13
K	91		59	285		1
K <sub>2</sub> SO <sub>4</sub>			407,959	296,285	277,143	7
NaHCO <sub>3</sub>			158,756	129,727	124,284	5
Na <sub>2</sub> CO <sub>3</sub> , total		6,768,470	6,396,526		6,350,260	13
Synthetic	3,991,592	3,929,904	3,878,194	3,985,242	4,118,597	7
NaCl					39,008,740	85
NaCl (Solar)			2,350,000			6
NaCl (Solution Mining)			5,928,000			?
Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> (& Chromate)		124,284	125,191	139,706	138,798	6
NaOH	9,797,544	9,196,084	9,276,006	9,199,712	8,996,504	62
Na			138,799	155,128	149,685	5
Sodium Silicate		601,460	569,709	569,709	596,017	33
Na <sub>2</sub> SO <sub>4</sub>		1,236,486	1,230,136	1,245,558	1,341,719	40
Na <sub>2</sub> SO <sub>3</sub>			185,065	222,259	205,930	6
H <sub>2</sub> SO <sub>4</sub>	29,664,786	27,257,130	26,691,000	26,784,489	26,795,375	150
TiO <sub>2</sub>	644,098	623,233	615,068	594,203	602,367	14



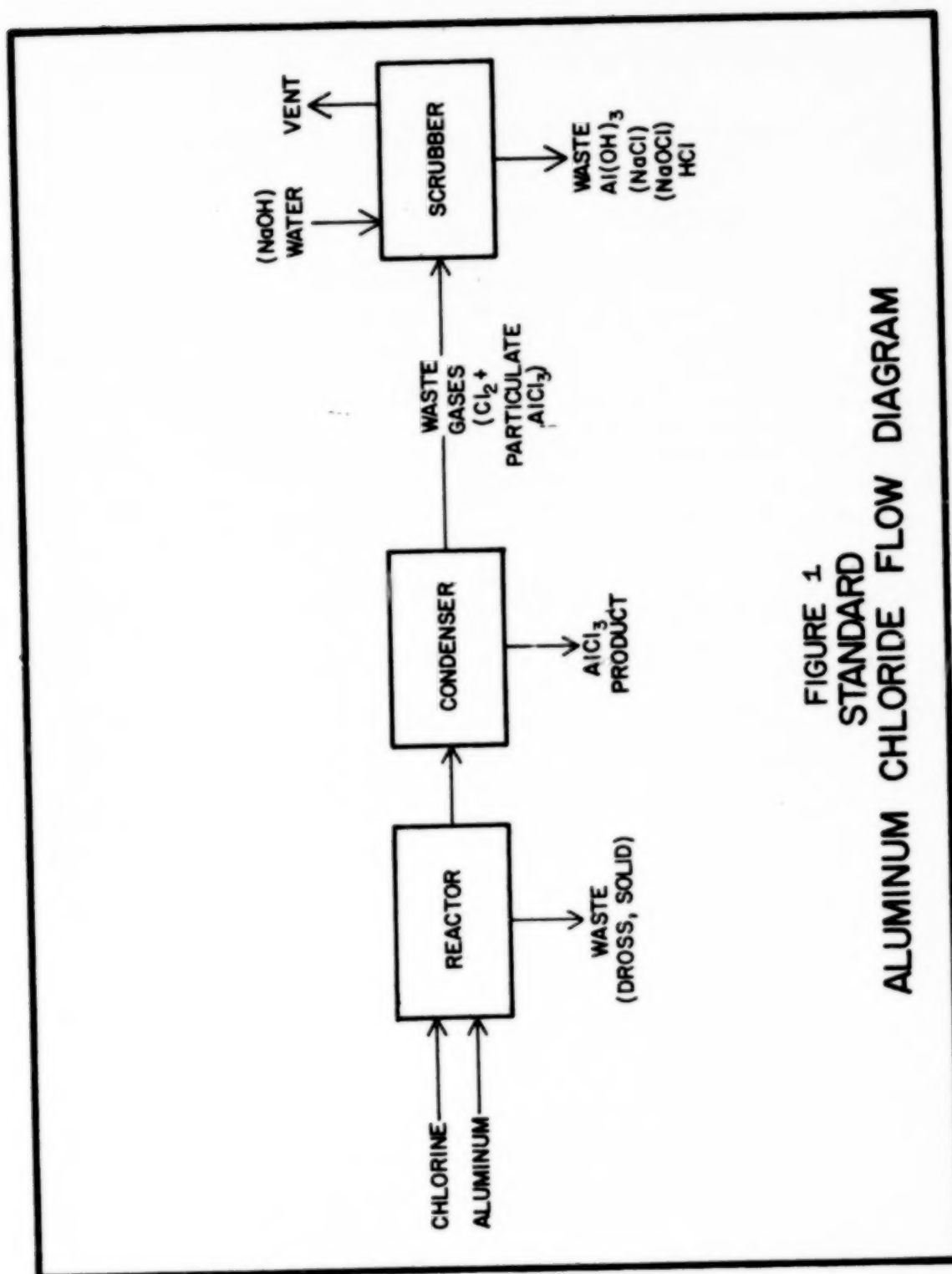


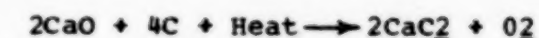
FIGURE 1  
STANDARD  
ALUMINUM CHLORIDE FLOW DIAGRAM

Ground ore and acid are reacted in a digester, from which the products, aluminum sulfate in solution plus muds and other insoluble materials from the ore, are fed into a settling tank. The aluminum sulfate solution is then clarified and filtered to remove any remaining insolubles. It may be sold as solution or evaporated to yield a solid product. A typical process diagram is shown in Figure 2.

Annual U.S. production in 1971 was 1,084,080 kkg (1,195,000 tcns). Aluminum sulfate, or filter alum, is used for water treatment (flocculation and clarification) and in treatment of paper mill waste, sewage, and other waste streams.

#### Calcium Carbide

This chemical is prepared by the reaction of calcium oxide with carbon (in the form of coke, petroleum coke, or anthracite) at 2000-2200°C (3632-3992°F) in a furnace similar to the familiar arc furnace, as shown in Figure 3. The general equation for the reaction is:



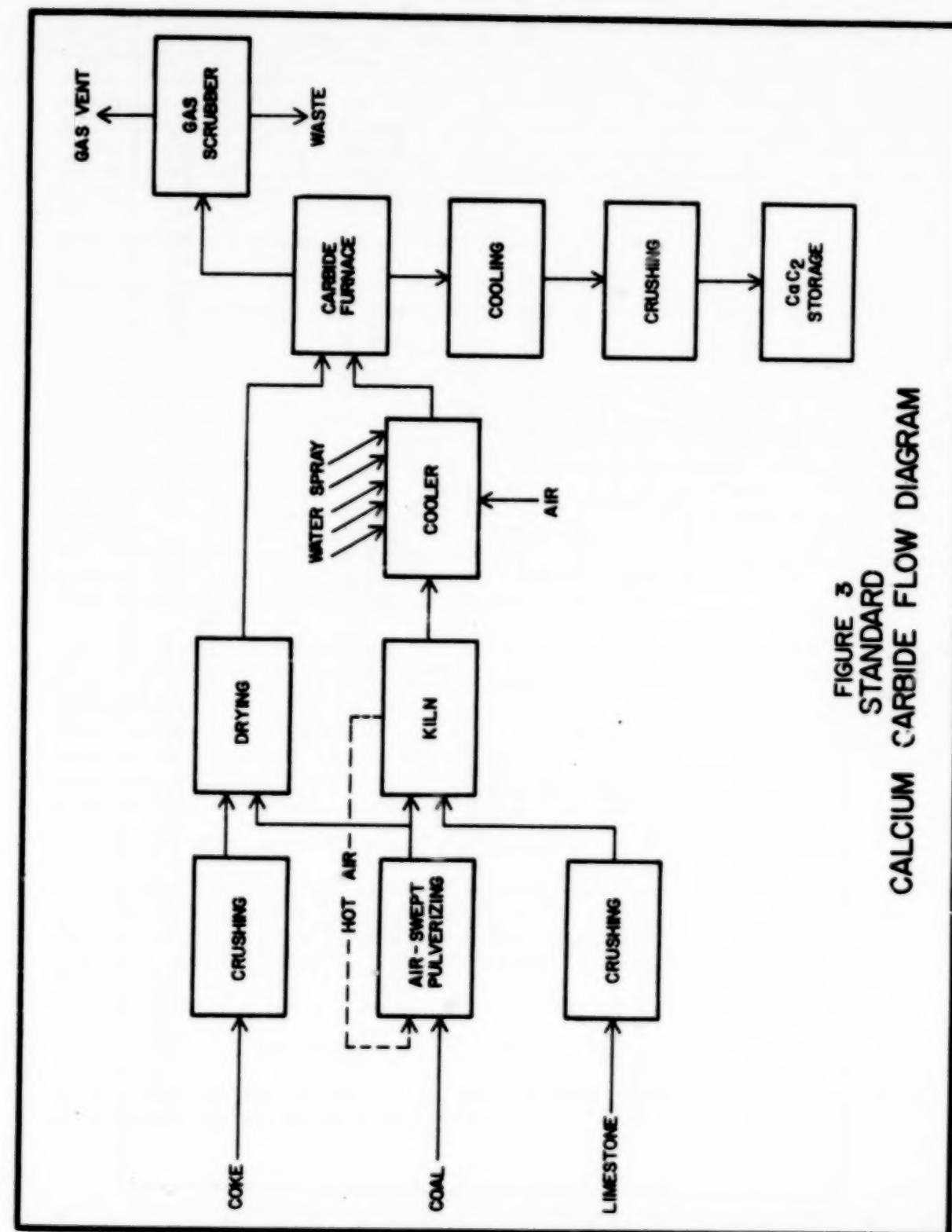
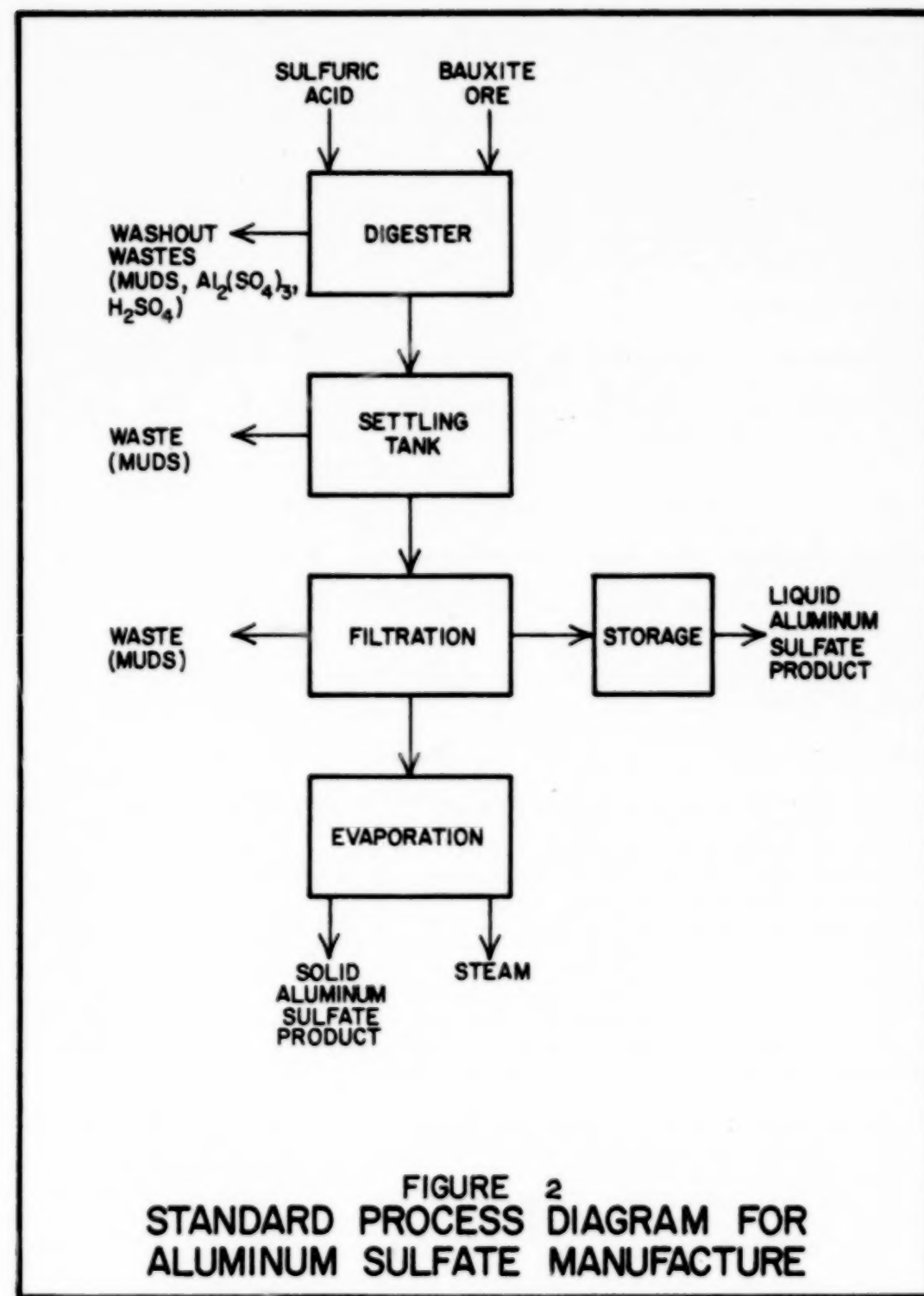
Calcium carbide is used primarily in the manufacturing of acetylene (by reaction with water). This use and the tonnage production has been steadily decreasing. Still, many calcium carbide plants are located in conjunction with acetylene plants. Since the production process is dry, the only major discharges are those effluents from scrubbing furnace and kiln offgases. The U.S. production in 1971 was 567,182 kkg (625,338 tons).

#### Calcium Chloride

Most of the calcium chloride produced is extracted from impure natural brines, but some of this salt is recovered as a by-product of soda ash manufacture by the Solvay process. In the manufacturing of calcium chloride from brine, the salts are solution mined and the resulting brines are first concentrated to remove sodium chloride by precipitation and then purified by the addition of other materials to precipitate sodium, potassium, and magnesium salts. The purified calcium chloride brine is then evaporated to yield a wet solid which is flaked and calcined to a dry solid product. Extensive recycling of partially purified brine is used to recover most of the sodium chloride values. A standard process diagram is shown in Figure 4.

Manufacture of calcium chloride from Solvay process waste liquors is similar to the natural brine process, except that the stepwise concentration and purification is unnecessary because no magnesium is present. Evaporation and calcining procedures are similar to those above. Significant wastes result from calcium chloride manufacturing.





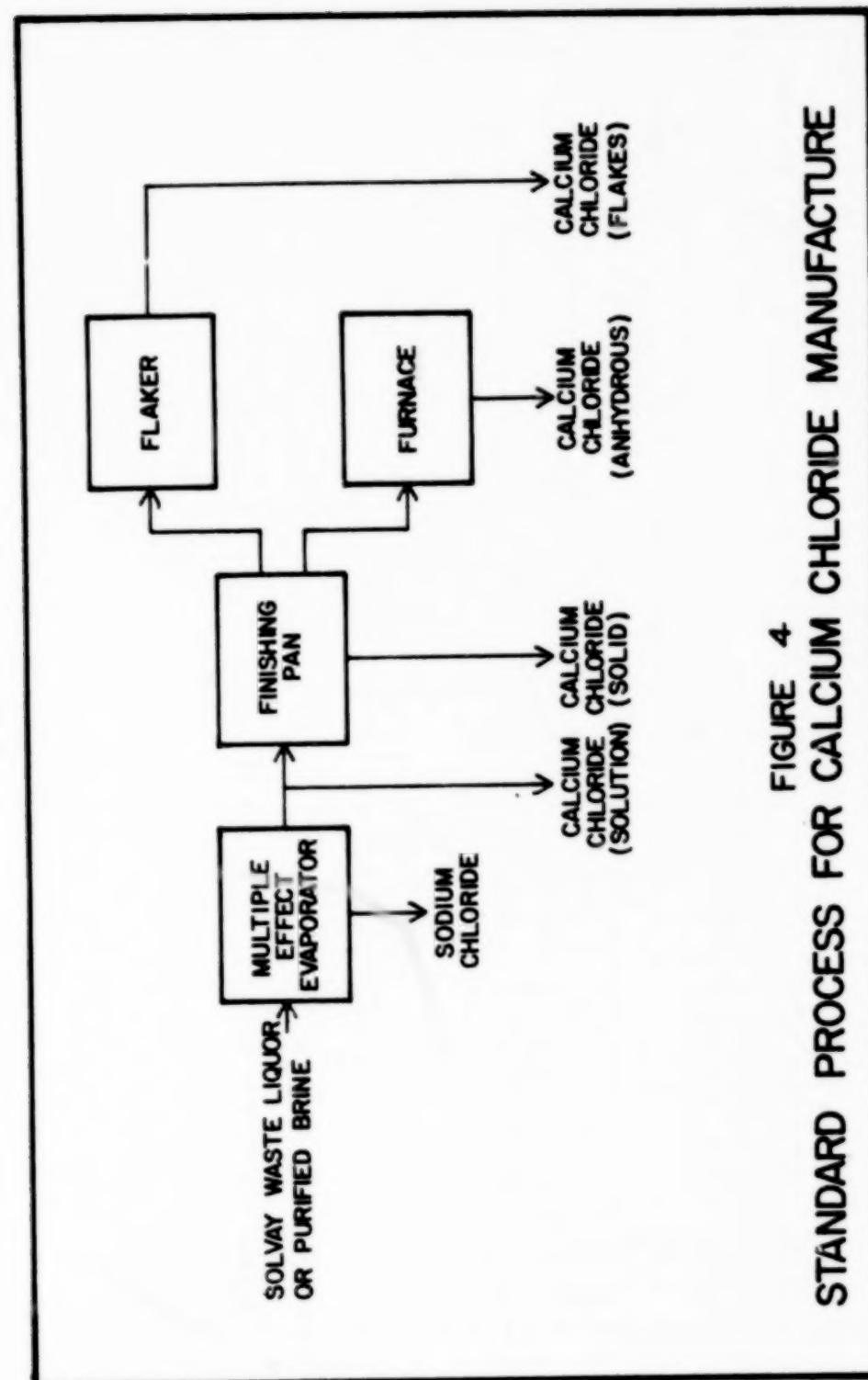
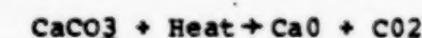


FIGURE 4  
STANDARD PROCESS FOR CALCIUM CHLORIDE MANUFACTURE

In 1971, U.S. production of calcium chloride was 1,101,281 kkg (1,213,000 tons). Uses include de-icing of roads, use as a stabilizer in pavement and cement, and dust control on roads. Production is increasing as more uses and markets are found, but potential production capability is much greater than that presently utilized. Recently, increased recovery resulting from pollution abatement measures has tended to cause calcium chloride supply to exceed demand. Plants recovering this salt from natural brines are located near mixed salt deposits, such as those in Michigan, West Virginia, and California.

#### Calcium Oxide and Calcium Hydroxide

Calcium oxide is produced by calcining various types of limestone in a continuous vertical or rotary kiln. The general equation for the reaction is:

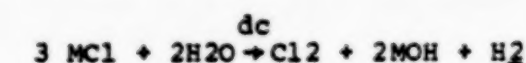


Formerly coal or coke was used as fuel in vertical kilns, but in recent years large gas-fired kilns have been widely used. After calcination, the calcium oxide is cooled and then packaged or crushed and screened to yield a pulverized product. It may be slaked by reaction with water to yield calcium hydroxide and then marketed. The only waterborne wastes result from wet scrubbing of the gaseous kiln effluent to remove particulates. These wastes are high pH liquors which also contain suspended solids. The standard process diagram is shown in Figure 5.

Annual U.S. production of lime is believed to total about 16,000,000 kkg (17,600,000 tons). Approximately 20 percent of this production is "captive" (made and consumed in the same facility), primarily in the sugar, alkali, and steel industries. The remainder finds a variety of chemical and industrial uses, including use as an alkali and use in hydrated lime manufacturing. Principal growth areas appear to be in basic oxygen steel production and in soil stabilization.

#### Chlorine, Sodium or Potassium Hydroxide

The major chlorine production results from the electrolysis of sodium or potassium chloride brines, in which caustic soda (NaOH) or caustic potash (KOH), respectively, are also produced. The general equation for the electrolysis is (where M can be either Na or K):



From the above equation it can be seen that hydrogen is also a by-product of brine electrolysis.

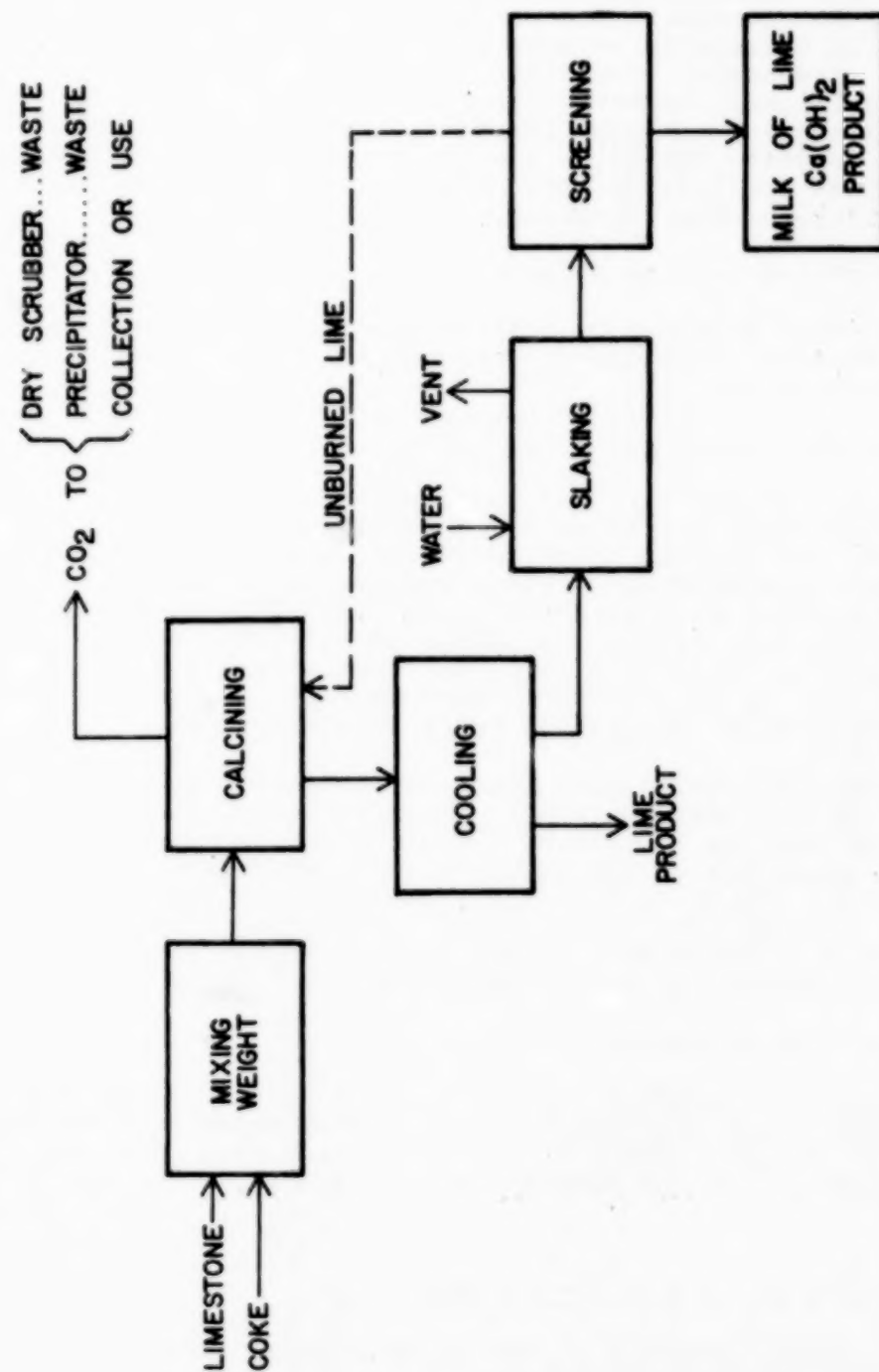


FIGURE 5  
STANDARD  
CALCIUM OXIDE (LIME) FLOW DIAGRAM

Other sources (minor in size) of chlorine include the manufacture of hydrochloric acid and metallic sodium.

Two types of electrolysis cells are used, mercury cells and diaphragm cells.

#### a) Diaphragm cell process

In the diaphragm cell process, Figure 6, sodium chloride brines are first purified by addition of sodium carbonate, lime flocculating agents and barium carbonate in the amounts required to precipitate all the magnesium, calcium and sulfate contents of the brine. The brine is filtered to remove the precipitated materials and is then electrolyzed in a diaphragm cell. Chlorine, formed at one electrode, is collected, cooled, dried with sulfuric acid, then purified, compressed, liquified and shipped. At the other electrode, sodium hydroxide is formed and hydrogen is liberated. The hydrogen is cooled, purified, compressed and sold and the sodium hydroxide formed, along with unreacted brine, is then evaporated at 50 percent concentration. During partial evaporation, most of the unreacted sodium chloride precipitates from the solution, which is then filtered. The collected sodium chloride is recycled to the process and the sodium hydroxide solutions are sold or further evaporated to yield solid products.

In cases where potassium hydroxide is manufactured as a co-product with chlorine, purified potassium chloride is used instead of sodium chloride as the starting material. Otherwise, the process is identical.

#### b) Mercury cell process

Figure 7 shows a standard process diagram for sodium hydroxide and chlorine production by the mercury cell process. The raw material salt, is dissolved and purified by addition of barium chloride, soda ash, and lime to remove magnesium and calcium salts and sulfates prior to electrolysis. The insolubles formed on addition of the treatment chemicals are filtered from the brine and the brine is fed to the mercury cell, wherein chlorine is liberated at one electrode and a sodium-mercury amalgam is formed at the other.

Mercury cells utilize mercury flowing along the bottom of a steel trough as the cathode. A multiple anode is comprised of horizontal graphite plates. Upon electrolysis the alkali metal forms an amalgam with the mercury. The amalgam is decomposed externally to the cell by the addition of water, which results in the formation of hydrogen.

The chlorine gas from the cells is collected, cooled, dried by contact with sulfuric acid, and then purified and liquified for





shipment, utilized on-site, or sold as gaseous chlorine. Much of the unreacted salt in the brine is recycled. Besides potential caustic and brine effluents some mercury is present in the spent brine from the mercury cell process. The cost of removing mercury from the effluent accounts, to some extent, for the shift back toward the diaphragm cells. Mercury cells began to be widely used in the early 1950's and reached a high of almost 30 percent of the total production in 1968.

The U.S. production of chlorine in 1971 totalled 8,482,660 kkg of gas (9,352,437 tons) and 4,035,489 kkg of liquid (4,449,271 tons). At present, about 75 percent of the production is in diaphragm cells, 20 percent in mercury cells, and 5 percent from other sources. About two-thirds of the production is utilized in the synthetic organic chemical and plastics industries, and half of that remaining is utilized in the pulp and paper industry (as a bleaching agent). Other uses include the inorganic chemicals industry, municipal water and sewage treatment, and many others. Somewhat over half of the total production is "captive", primarily in the synthetic organic chemicals and the pulp and paper industries. In recent years proximity to markets has been the major factor in chlorine plant location, in contrast to the cost of power and salt which previously dominated plant economics.

Sodium hydroxide is produced from the electrolysis of sodium chloride brines in mercury or diaphragm cells as described above. The caustic solution from the cathode of the electrolysis cell is evaporated to about 50 percent by weight sodium hydroxide. This may be sold as "standard-grade caustic liquor", concentrated to 73 percent, or further refined through removal of chloride and chlorate by various techniques. Refined caustic liquor may be sold, further concentrated to 73 percent solids, or evaporated to dryness. The anhydrous sodium hydroxide is sold in solid (flake or powdered) forms. Most of the product is sold in the liquid form.

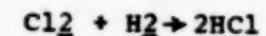
Caustic soda has many varied uses, mostly as an alkali. It has also replaced soda ash (sodium carbonate) in many uses, such as in the aluminum industry and in other molten salt processes. It is used to manufacture soda ash in one plant. In 1971, the U.S. production of sodium hydroxide was 8,780,946 kkg (9,681,397 tons) in liquid form and 493,393 kkg (543,983 tons) in solid form.

Production methods for potassium hydroxide are very similar to those for sodium hydroxide, except that mined potassium chloride brines are used as the raw material. In the mercury cell process, the potassium-mercury amalgam is decomposed with water. The mercury is recycled and the caustic solution is cooled and filtered to recover potassium hydroxide.

The U.S. production of potassium hydroxide in 1971 was 179,760 kkg (198,192 tons). Caustic potash is used as an alkali, particularly when very high purity is desired or where other factors allow it to compete with sodium hydroxide (captive production, for instance). Other uses include the manufacturing of potassium salts and organic compounds containing potassium.

#### Hydrochloric Acid

There are two major processes used for hydrochloric acid manufacture. The process considered in this Document, as shown in Figure 8, is direct reaction of chlorine with hydrogen by:



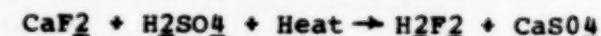
The second major source of production for hydrochloric acid, as a by-product of organic chlorination reactions, is the dominant source. This process is beyond the scope of this Document. By-product hydrochloric acid is typically of lower purity than that produced by direct reaction.

In the production of hydrochloric acid by direct reaction, hydrogen and chlorine gases are reacted in a vertical burner. The product hydrogen chloride so formed is cooled and then absorbed in water. Exhaust gases are scrubbed, and acid values are recycled. End products may include strong acid (22°Be) from the cooler, weak acid (18°Be) from the absorber column, a mixture of these (20°Be), or anhydrous HCl. The anhydrous acid may be prepared by stripping gaseous HCl from strong acid. The condensate and column bottoms from this process may then be recycled back into the hydrochloric acid recovery process.

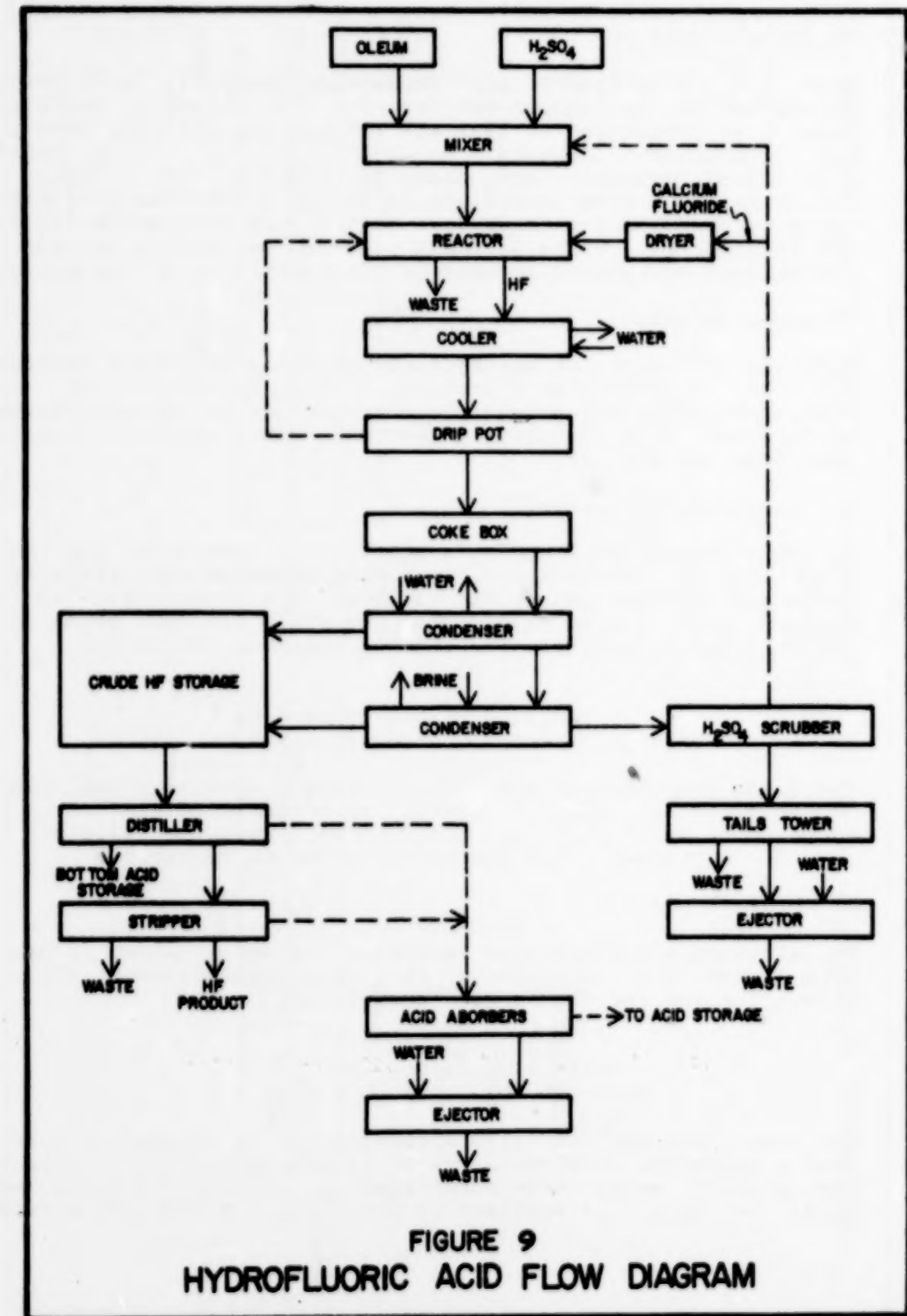
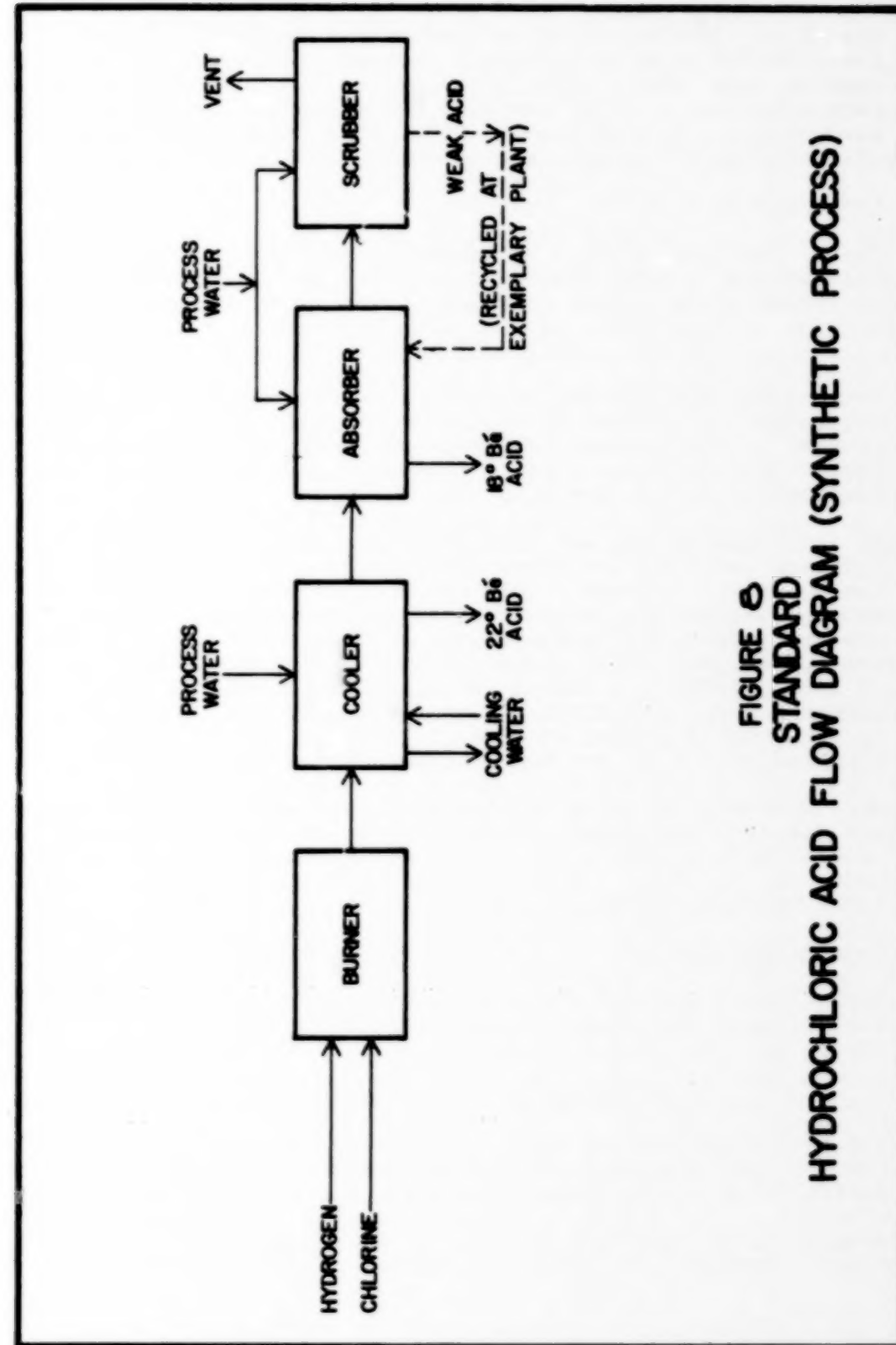
Approximately 90 percent of the current production is byproduct, and supply often exceeds demand. Uses include pickling of steel, chlorination reactions (in place of chlorine), and a variety of uses as an acid agent. Total U.S. production in 1971 was 1,904,075 kkg (2,099,371 tons).

#### Hydrofluoric Acid

Hydrofluoric acid is obtained by reacting the mineral fluor spar ( $\text{CaF}_2$ ) with concentrated sulfuric acid in a furnace, as shown in Figure 9. The general reaction for this process is:



The hydrofluoric acid leaves the furnace as a gas, which is then cooled and absorbed in water prior to purification. In the purification system, the crude acid is redistilled and either absorbed in water to yield aqueous hydrofluoric acid or compressed and bottled for sale as anhydrous hydrofluoric acid. Final drying of the anhydrous gas is accomplished with





concentrated sulfuric acid. Aqueous acid is normally shipped as 70 percent acid.

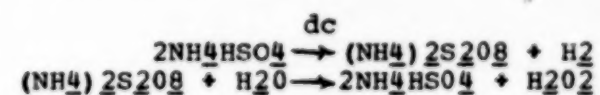
Most U.S. hydrofluoric acid production (probably 75-80 percent) is captive to the fluorinated organics and plastics industries. Total U.S. production in 1971 was 199,069 kkg (219,481 tons), and the production appears to be increasing fairly rapidly. Fluorinated organics and plastics comprise the major use industries. Another major use is in the production of synthetic cryolite and aluminum fluoride. Most of the acid-grade fluorspar ore is imported. Waste disposal problems and safety hazards are specialized and severe because of the reactivity of the material.

#### Hydrogen Peroxide

Hydrogen peroxide is manufactured by three different processes: (1) An electrolytic process; (2) Oxidation of alkyl hydroanthraquinones; and (3) As a by-product in the manufacturing of acetone from isopropyl alcohol. This Document includes processes (1) and (2).

##### a) Electrolytic process

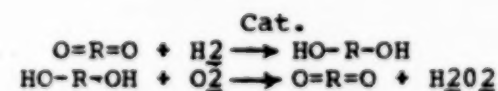
In the electrolytic process, a solution of ammonium (or other) bisulfate is electrolyzed, yielding ammonium persulfate at the anode and hydrogen gas at the cathode. The persulfate is then reacted with water (hydrolyzed) to yield hydrogen peroxide and the original bisulfate. The general reaction scheme is:



The crude peroxide product emerges mixed with water, and can be concentrated to desired levels by vacuum distillation or low-temperature fractionation. The cathode liquor is filtered and reused. A standard flow diagram is shown in Figure 10.

##### b) Organic process

The alkylhydroanthraquinone oxidation process is shown in general form below ("R" represents the alkylanthraquinone molecule, except for the two double-bonded oxygens):



In this process, the alkylanthraquinone is reduced by hydrogen over a supported metal catalyst (typically palladium on alumina), the product being the corresponding alkylhydroanthraquinone. This, in turn, is oxidized by oxygen in a forced gas stream to

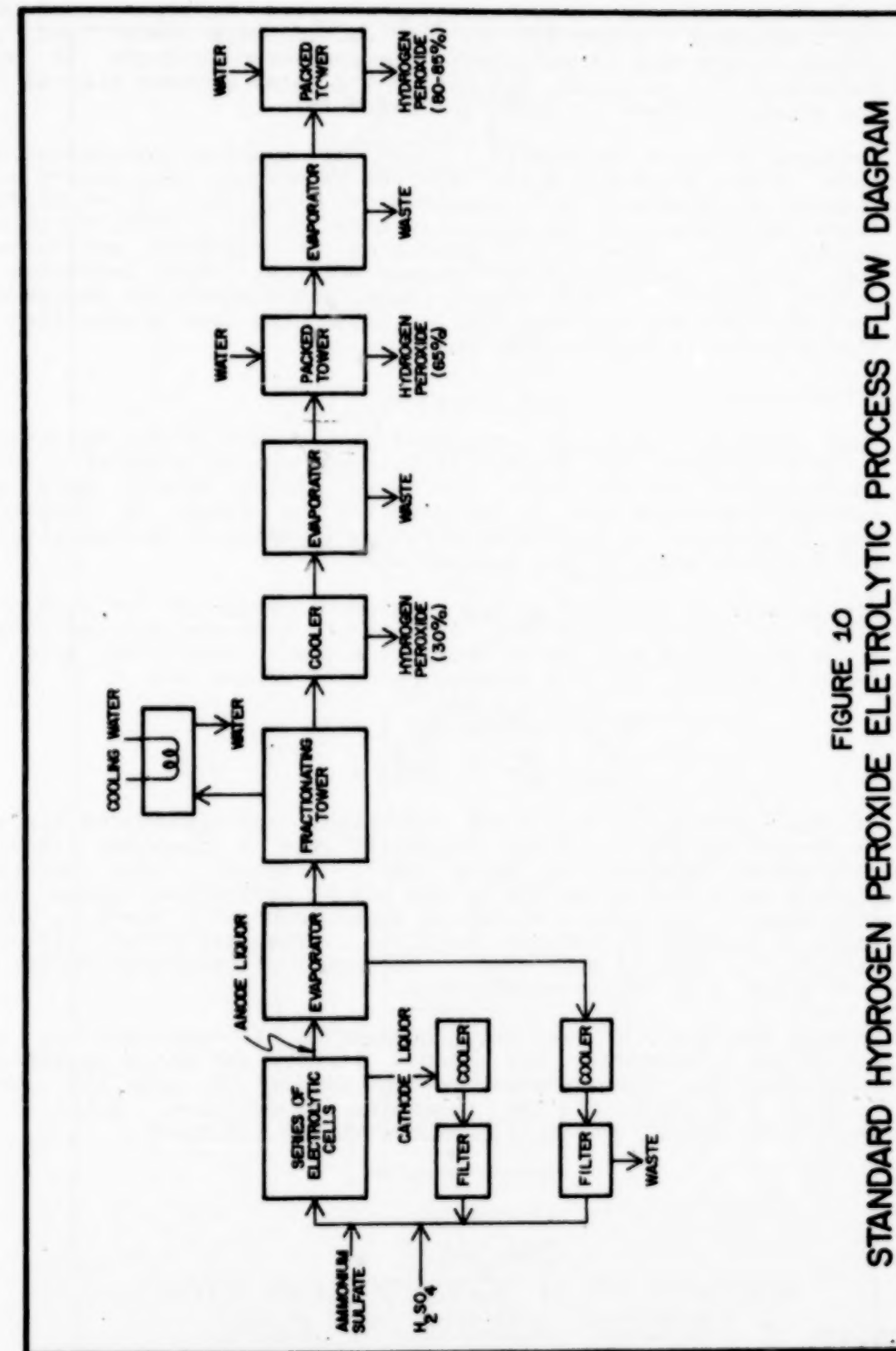


FIGURE 10  
STANDARD HYDROGEN PEROXIDE ELECTROLYTIC PROCESS FLOW DIAGRAM

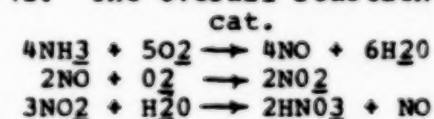
reform the original alkylanthraquinone plus hydrogen peroxide. The hydrogen peroxide is extracted with water and the alkylanthraquinone is recycled. The recovered product is then concentrated, purified, and sold. A general process diagram for the organic process is shown in Figure 11.

Hydrogen peroxide is sold in a range of aqueous concentrations from three percent to 98 percent by weight. The higher concentration materials are dangerously reactive. A stabilizer (such as acetanilid) is typically added to the product to retard decomposition. Uses include bleaching of textiles and paper, epoxidation, production of peroxy-acid catalysts, oxidation of organic compounds, formation of foams, and a source of energy for both military and civilian applications. The U.S. production in 1971 was 57,937 kkg (63,878 tons).

#### Nitric Acid

This document covers production of nitric acid in concentrations up to 68 percent by weight (azetropic concentration). More concentrated nitric acid, including fuming nitric acid and nitrogen pentoxide will be included in the Phase II Document. The production of nitric acid by the reaction of sodium nitrate and sulfuric acid is also not included.

Nitric acid is produced by the catalytic oxidation of ammonia, first to nitric oxide (NO), and then to nitrogen dioxide (NO<sub>2</sub>), which is reacted with water under pressure to form the acid as shown in Figure 12. The overall reaction scheme is:



In the process, compressed, purified, and preheated air and anhydrous ammonia are mixed and passed over a platinum rhodium wire-gauze catalyst at about 750°C (1382°F). The resultant mixture of nitric oxide and excess air is introduced, along with additional air, into a stainless steel absorption tower in which the nitric oxide is further oxidized. The resulting nitrogen dioxide is reacted with water. The bottom of the tower yields 61 - 65 percent by weight nitric acid.

Most of the U.S. nitric acid production is utilized in the fertilizer industry. The second largest use is in explosives manufacturing. Various uses as an acidic or pickling agent account for much of the remaining production. Total U.S. production in 1971 was 6,151,112 kkg (6,742,130 tons).

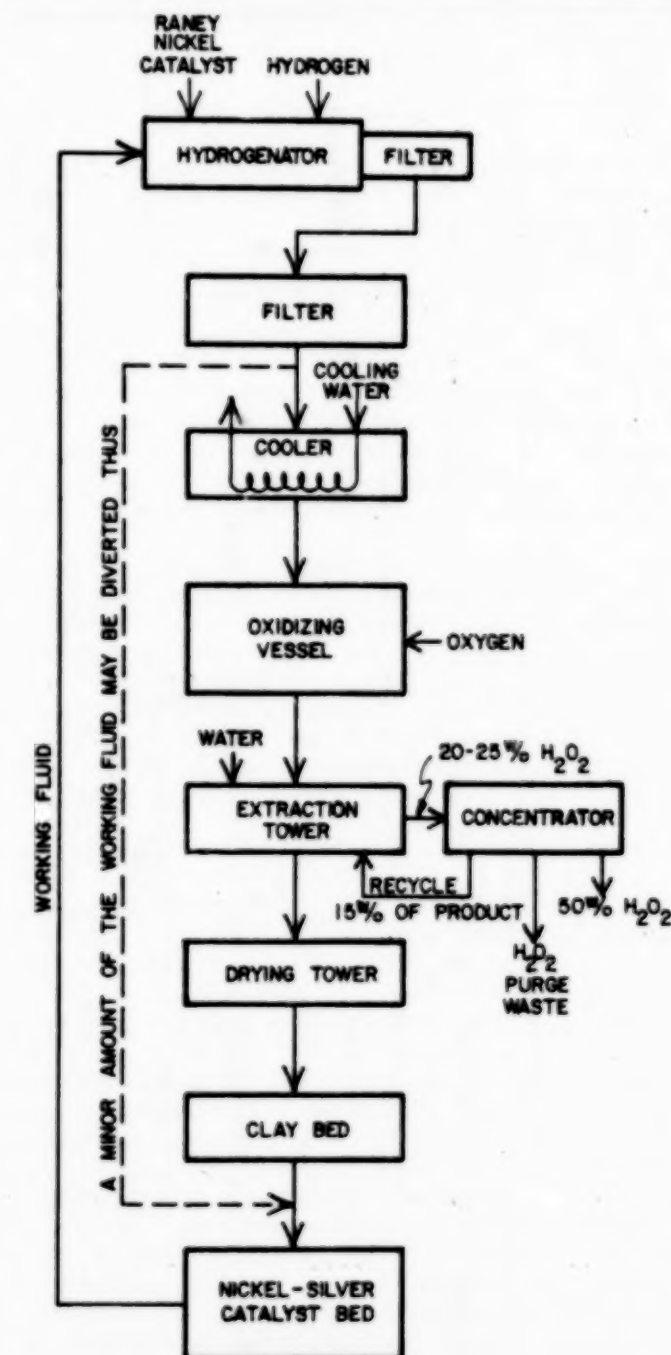


FIGURE 11  
STANDARD  
HYDROGEN PEROXIDE FLOW DIAGRAM  
(RIEDL-PFLEIDERER PROCESS)

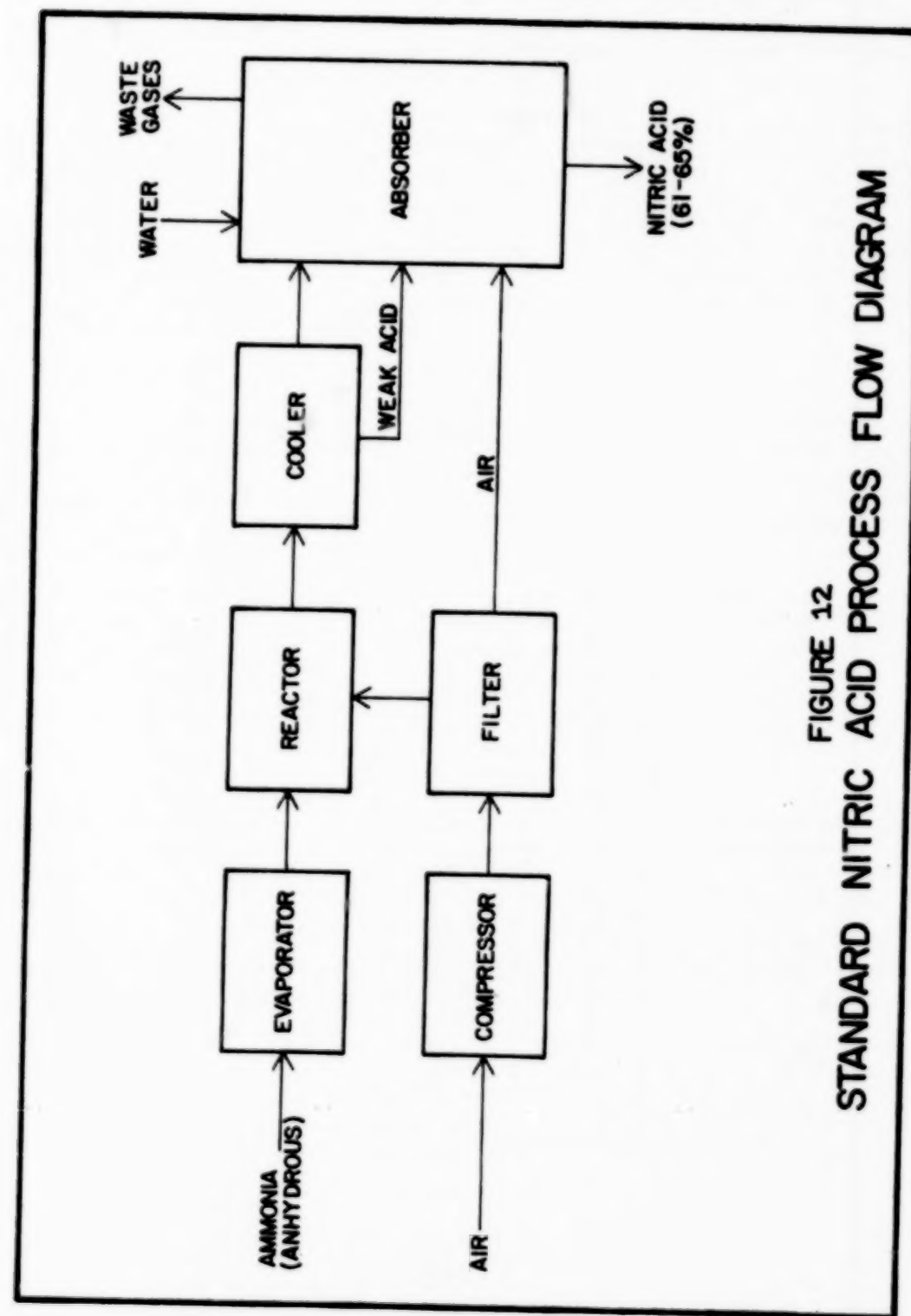
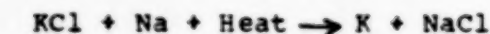


FIGURE 12  
STANDARD NITRIC ACID PROCESS FLOW DIAGRAM

#### Potassium Metal

Potassium is produced by the reaction of potassium chloride with sodium vapor:

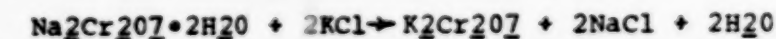


For the commercial preparation of potassium metal, potassium chloride is melted in a gas fired melt pot and fed to an exchange column as shown in Figure 13. The molten potassium chloride flows over Raschig rings in the packed column, where it contacts ascending sodium vapors coming from a gas-fired reboiler. An equilibrium is established between the two, yielding sodium chloride and elemental potassium. The sodium chloride formed is continuously withdrawn at the base of the apparatus and is normally sold. The column operating conditions may be varied to yield either pure potassium metal as an overhead product or to vaporize sodium along with the potassium to produce sodium-potassium (NaK) alloys of varying compositions. Potassium metal of over 99.5 percent purity can be continuously produced.

Since it is relatively more reactive than sodium, the reaction between potassium and carbon (plus a tendency to form explosive carbonyls) precludes the manufacture of potassium by electrolysis. Because it is more expensive than sodium, potassium has very limited uses. Major uses include manufacture of organo-potassium compounds and production of NaK (sodium potassium alloys used in lard modification and as a nuclear reactor coolant). Total U.S. production in 1972 was about 100 kkg (110 tons), primarily from one facility.

#### Potassium Dichromate

Most of the potassium dichromate manufactured in the U.S. is made by reacting a sodium dichromate dihydrate solution with potassium chloride according to the following:



Potassium chloride is added to a dichromate solution, which is then pH adjusted, saturated, filtered and vacuum cooled to precipitate crystalline potassium dichromate which is recovered by centrifuging, dried, sized and packaged. The mother liquor from the product centrifuge is then concentrated to precipitate sodium chloride which is removed as a solid waste from a salt centrifuge. The process liquid is recycled to the initial reaction tank. Figure 14 is the standard process diagram. A relatively pure product results which requires only removal of the water prior to sizing and packaging.

The major uses of potassium dichromate are as a glass pigment and a photographic development chemical. Estimated annual production in the U.S. is 4,000-4,500 kkg (4,400-5,000 tons).



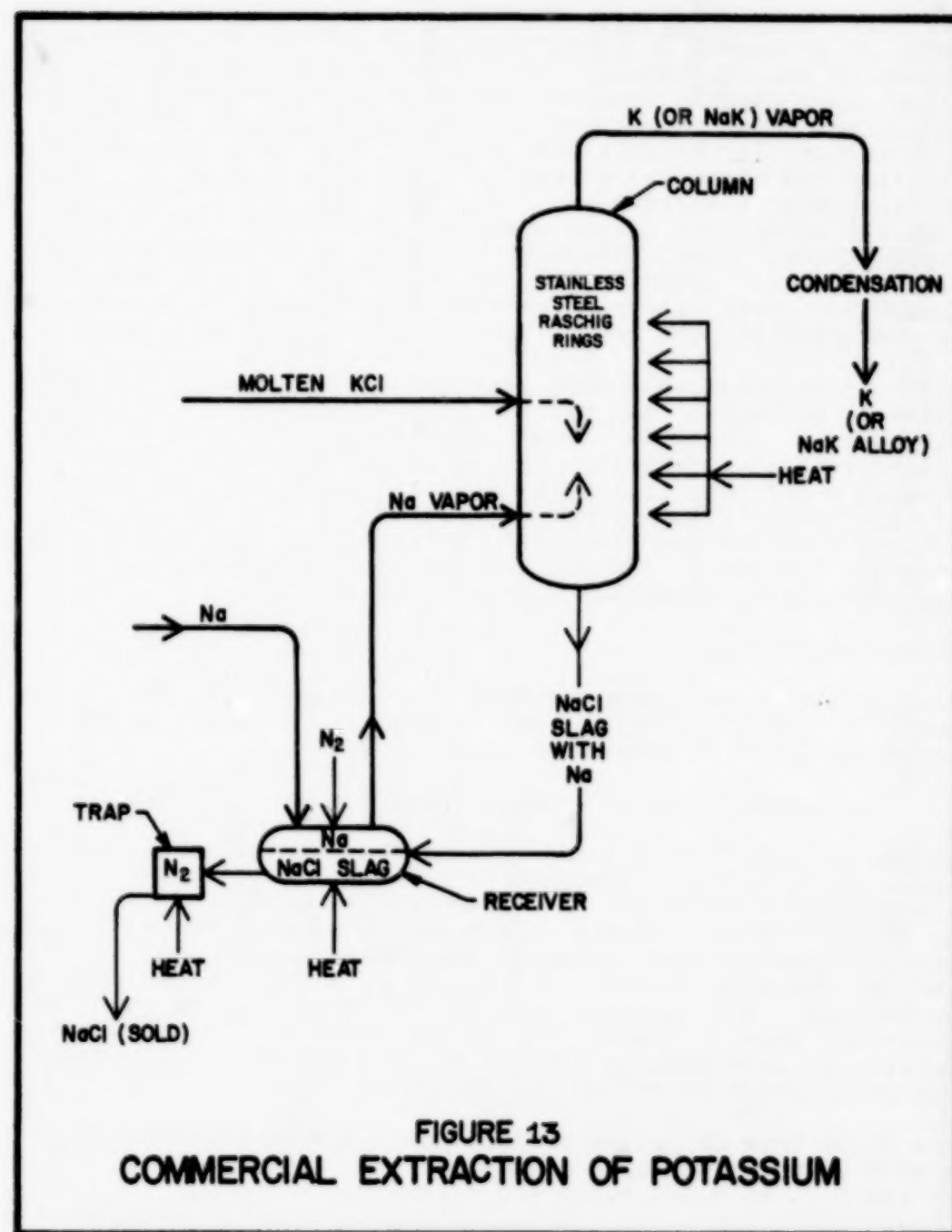


FIGURE 13  
COMMERCIAL EXTRACTION OF POTASSIUM

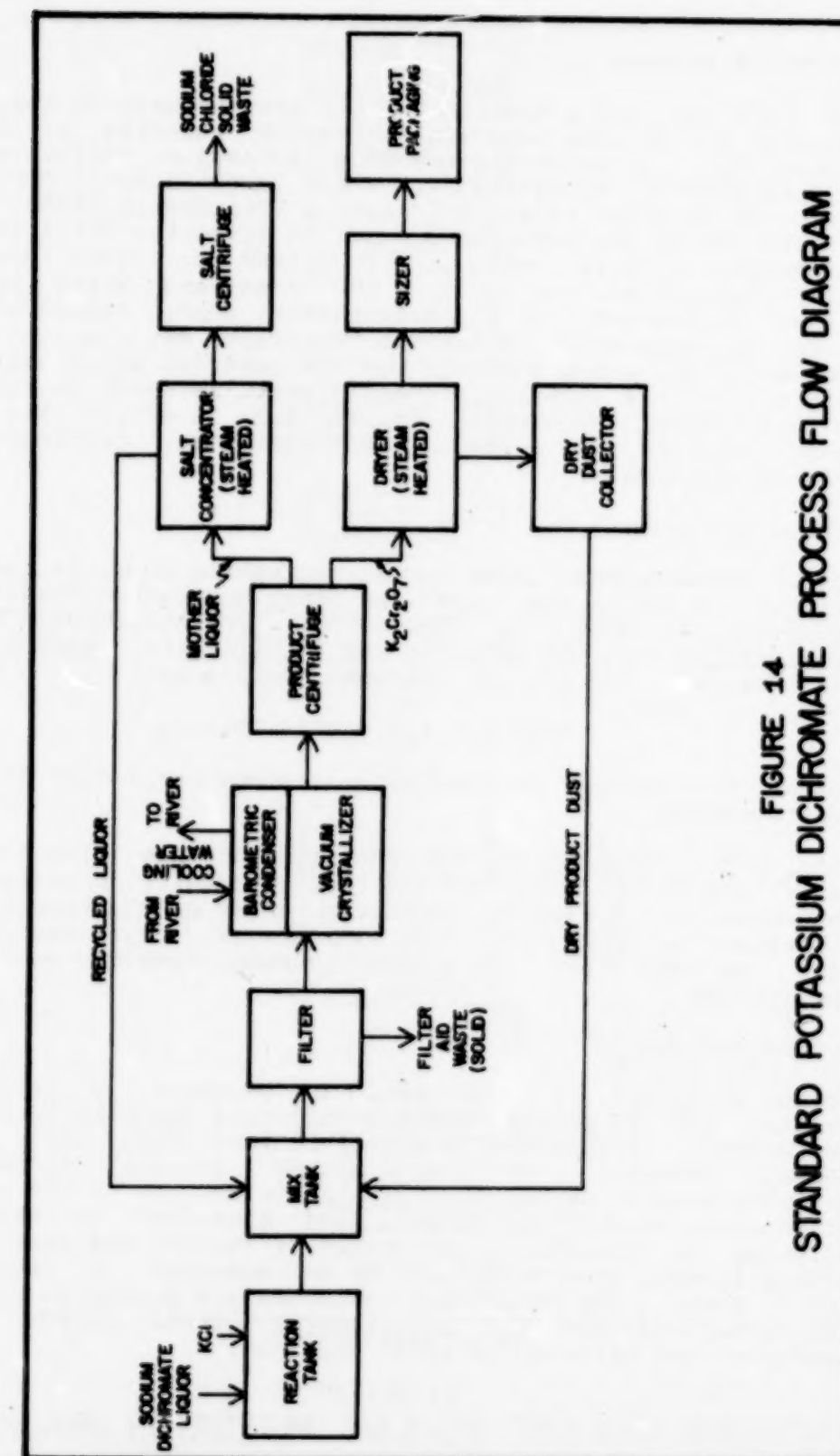


FIGURE 14  
STANDARD POTASSIUM DICHROMATE PROCESS FLOW DIAGRAM

## Potassium Sulfate

The bulk of the potassium sulfate manufactured in the U.S. is prepared by the treatment with potassium chloride of dissolved langbeinite, a naturally-occurring potassium sulfate-magnesium sulfate mineral,  $K_2SO_4 \cdot 2MgSO_4$ . Mined langbeinite is crushed and dissolved in water to which potassium chloride is added. Partial evaporation of the solution results in selective precipitation of potassium sulfate which is recovered by centrifugation or filtration, dried, and sold. The remaining brine liquor is either discharged to an evaporation pond, reused as process water, or evaporated. Magnesium chloride may be economically recovered as a byproduct if the raw material is of sufficiently high quality. A standard process diagram is shown in Figure 15. Current annual production in the U.S. is 407,916 kkg (449,742 tons). Much of this finds agricultural use, particularly for tobacco and citrus.

## Sodium Bicarbonate

Sodium bicarbonate, also known as baking soda, is made by the reaction of sodium carbonate with water and carbon dioxide under pressure, as shown in Figure 16. The bicarbonate so formed precipitates from the solution and is filtered, washed, dried, and packaged. The general process reaction is:



Sodium bicarbonate is typically a minor by-product of soda ash manufacturers.

Total U.S. production in 1971 was 158,305 kkg (174,537 tons). Major industrial users include food processors, chemical plants, pharmaceutical producers, synthetic rubber manufacturers, leather processors and paper and textile producers. It is also used in fire extinguishers to form carbon dioxide and in food preparation.

## Sodium Carbonate

Sodium carbonate, or soda ash, is produced by the "Solvay" process and by mining naturally-occurring deposits in California and Wyoming. Production by mining is less than that from the Solvay process. In the mining process, trona (sodium sesquicarbonate,  $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ ) is brought to the surface in solid form, crushed and ground, and dissolved in water. The solution is clarified, thickened, filtered, and sent to vacuum crystallizers, from which part of the soda ash is recovered in solid form. The remaining solution is cooled to precipitate additional soda ash and bicarbonate. These solids are then dewatered and calcined to yield soda ash.

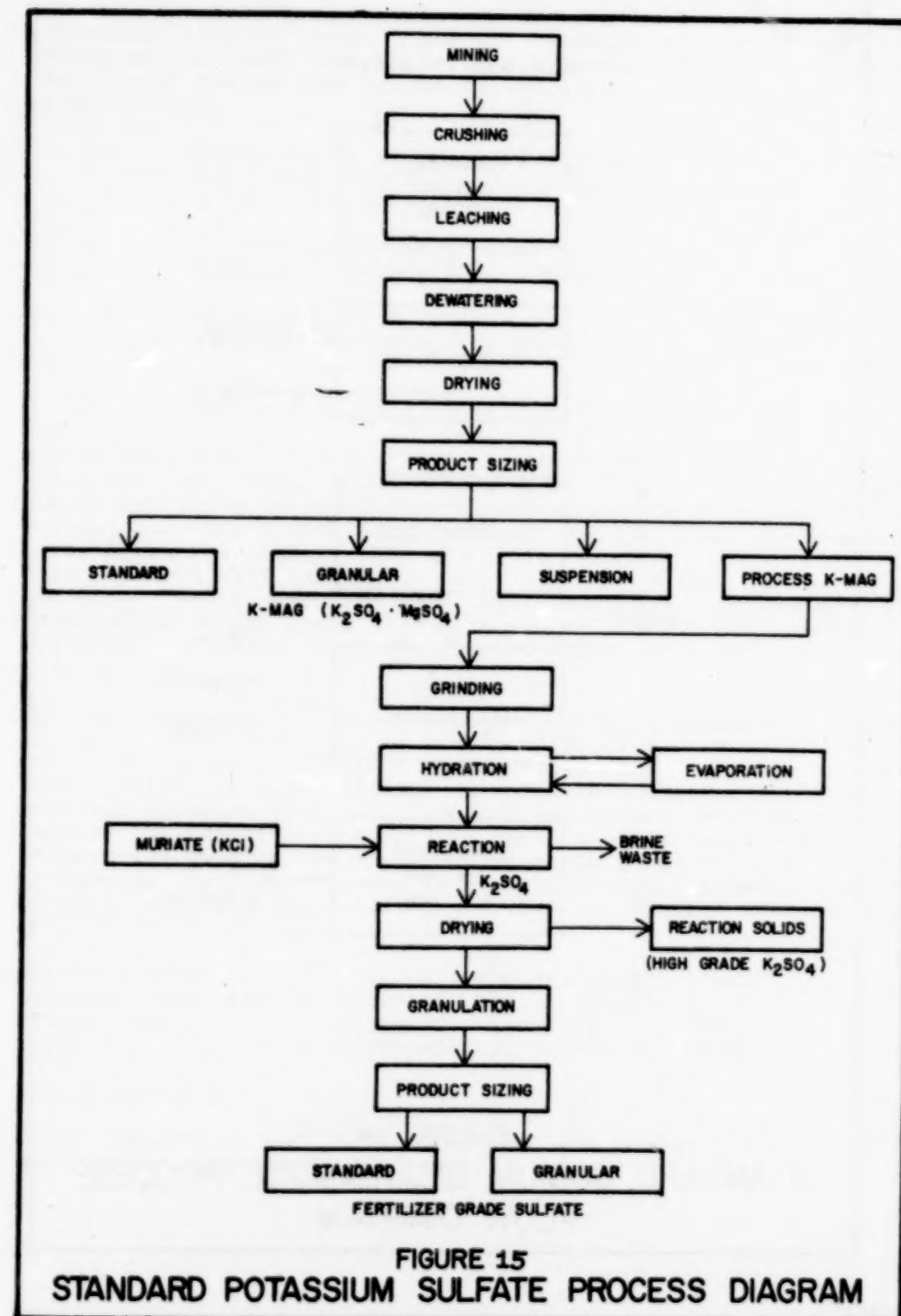


FIGURE 15  
STANDARD POTASSIUM SULFATE PROCESS DIAGRAM

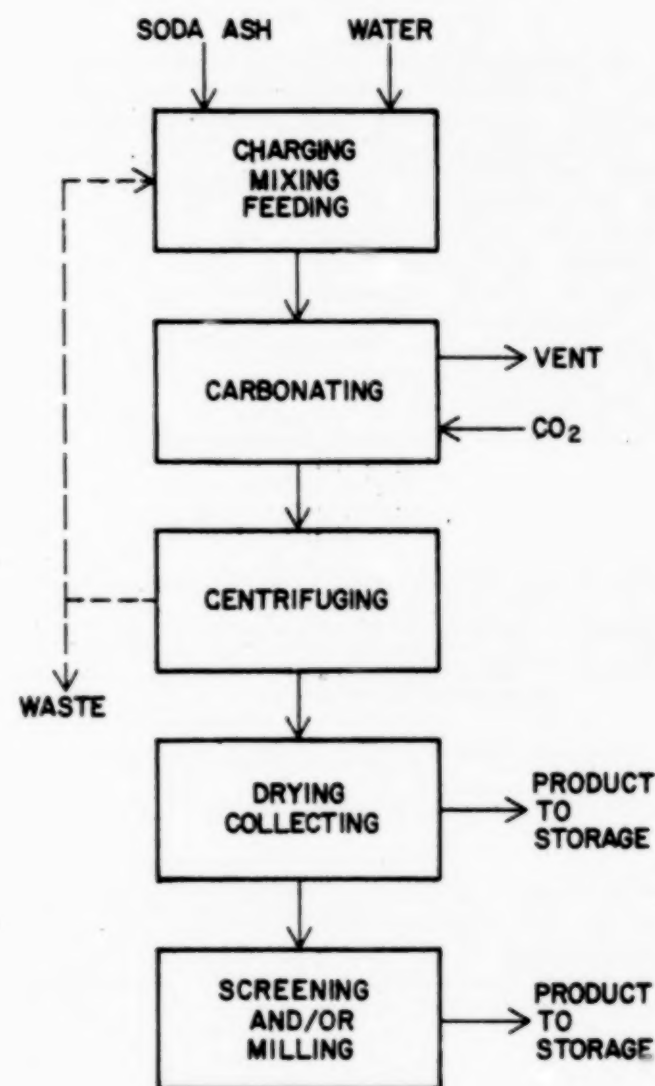
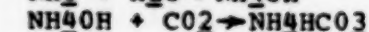
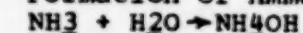


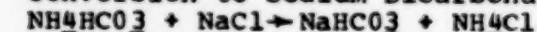
FIGURE 10  
STANDARD SODIUM BICARBONATE PROCESS  
FLOW DIAGRAM

The Solvay process, as shown in Figure 17, involves a reaction in aqueous solution (under pressure) between ammonia, brine (NaCl), and carbon dioxide to yield sodium bicarbonate, which is then converted to soda ash by heating. Ammonia is recovered by the addition of slaked lime to the used liquor. The general reaction is as follows:

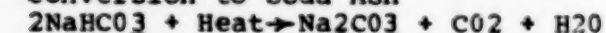
Formation of Ammonium Bicarbonate



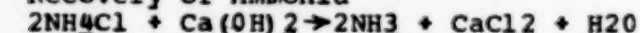
Conversion to Sodium Bicarbonate



Conversion to Soda Ash



Recovery of Ammonia



The saturated brine is purified of other metal ions by precipitation, and then picks up ammonia in an absorber tower. Ammoniated brine is reacted with carbon dioxide in a carbonating tower, and the resulting bicarbonate precipitates as the sodium salt, forming a slurry. The slurry is filtered to remove the solid bicarbonate which is calcined to yield the light ash product. Dense ash is made by successive hydration and dehydration of the light ash. The carbon dioxide and ammonia are recycled. Calcium chloride is also being recovered now in some plants.

Many soda ash plants are associated with producers of glass (largest user industry) or with sources or raw material such as coke-oven plants (by-product ammonia), the cement industry (utilization of lime sludge), or solid carbon dioxide producers. Soda ash competes with caustic soda and other chemicals in a variety of applications other than glass manufacture. Large amounts are used in the non-ferrous metals industry and in the production of bicarbonate and washing soda. Several types of products are sold commercially. Production figures for the U.S. in 1971 are as follows:

Finished Light Ash	-	1,676,621 kkg	(1,848,535 tons)
Finished Dense Ash	-	2,120,467 kkg	(2,337,891 tons)
Natural Ash	-	2,598,321 kkg	(2,864,742 tons)
Total	-	6,395,409 kkg	(7,051,168 tons)

Sodium Chloride

Large quantities of this chemical are produced from brine or seawater by three basic processes:



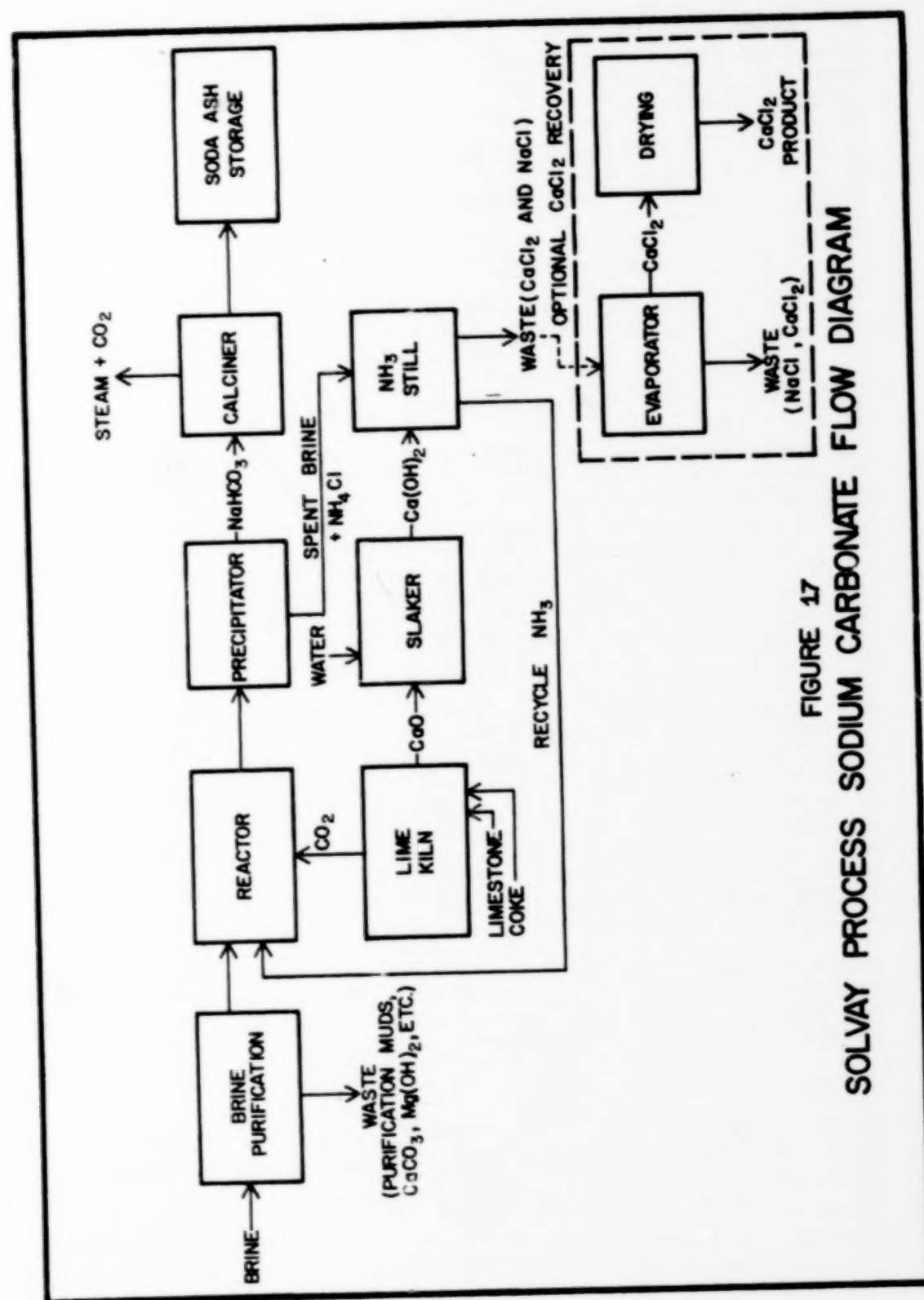


FIGURE 17  
SOLVAY PROCESS SODIUM CARBONATE FLOW DIAGRAM

- (1) solar evaporation of brine;
- (2) solution mining of natural salt; and
- (3) conventional mining of rock salt.

a) Solar evaporation process

In the solar evaporation process, salt water is concentrated by evaporation over a period of several years in open ponds to yield a saturated brine solution. After saturation is reached, the brine is then fed to a crystallizer, wherein sodium chloride precipitates, leaving behind a concentrated brine solution (bittern) consisting of sodium, potassium and magnesium salts. The precipitated sodium chloride is recovered for sale and the brine may be further evaporated to recover additional sodium chloride values and is either stored, discharged back to salt water or further worked to recover potassium and magnesium salts. A process diagram is shown in Figure 18.

b) Solution brine-mining process

Saturated brine for the production of evaporated salt is usually obtained by pumping water into an underground salt deposit and removing a saturated salt solution from an adjacent interconnected well, or from the same well by means of an annular pipe. Besides sodium chloride, the brine will normally contain some calcium sulfate, calcium chloride and magnesium chloride and lesser amounts of other materials.

The chemical treatment given to brines varies from plant to plant depending on impurities present. Typically, the brine may be first aerated to remove hydrogen sulfide and, in many cases, small amounts of chlorine are added to complete sulfide removal and oxidize all iron salts present to the ferric state. The brine is then pumped to settling tanks where it is treated with soda ash and caustic soda to remove most of the calcium, magnesium and iron present as insoluble salts. After clarification to remove these insolubles, the brine is then sent to multiple effect evaporators. As water is removed, salt crystals form and are removed as a slurry. After screening to remove lumps, the slurry is then washed with fresh brine. By this washing, fine crystals of calcium sulfate are removed from the mother liquor of the slurry and returned to the evaporator. Eventually the calcium sulfate concentration in the evaporator builds up to the point where it must be removed by "boiling out" the evaporators.

The washed slurry is filtered, the mother liquor is returned to the evaporators and the salt crystals from the filter are dried and screened. Salt produced from a typical brine will be of 99.8 percent purity or greater. Some plants do not treat the raw brine, but control the calcium and magnesium impurities by watching the concentrations in the evaporators and bleeding off

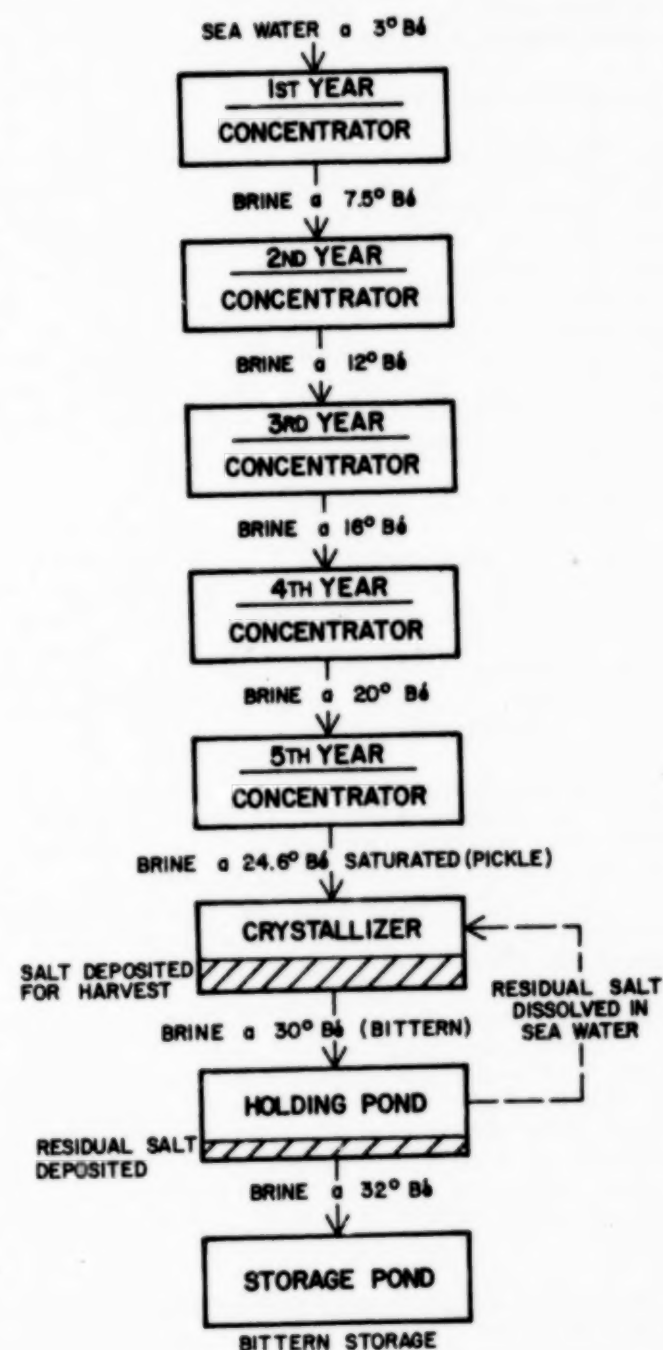


FIGURE 18  
STANDARD SOLAR SALT PROCESS  
FLOW DIAGRAM

sufficient brine to maintain a predetermined level. By such methods, salt of better than 99.5 percent purity can be made.

In either case, the final screening of the dried salt yields various grades depending on particle size. A detailed process diagram is shown in Figure 19.

In the "Grainer" system, saturated and pretreated brine from the above processes is heated in a flat, open pan (or grainer). Flat crystals of sodium chloride form on the quiescent surface of the solution and fall to the bottom of the grainer. There they grow until they are removed by a submerged rake system. Recovered crystals are subsequently washed, dried, classified as to size, and packed. Brine pretreatment allows sodium chloride purities of 99.98 percent by this method.

In the "vacuum pan" system, pretreated brine enters vacuum evaporators which remove water and allow sodium chloride crystals to precipitate out. The crystals are then washed, filtered, and dried prior to packing. The "Alberger" process is similar except that an open evaporator is used to remove water sufficiently to allow precipitation of salt crystals. These crystals are centrifuged to remove liquid, dried, and packed. The feed to the open evaporator includes saturated brine and a slurry of sodium chloride crystals in brine. This slurry is the liquid effluent from the evaporator with some of the water removed by evaporation.

A wide variety of solid products are available, with various particle sizes, solid forms, purities, and additives. Exact production figures are not available, but current annual production appears to be between 40,000,000 and 50,000,000 kkg (44,000,000 and 55,000,000 tons). Because salt sources are widespread and the product is relatively inexpensive, production facilities are localized and operated on a relatively low profit margin. Major salt deposits in the U.S. include a large bed extending from western New York through much of Michigan, brine wells in the Ohio Valley, a large bed under central Kansas and northern Oklahoma, and salt domes in Texas and Louisiana. In 1971 salt production by solar evaporation was 2,140,000 kkg (2,350,000 tons) and the production by solution mining was 5,390,000 kkg (5,928,000 tons). Practically all chemical compounds containing sodium or chlorine are derived from salt. The chemical industry utilizes almost all of the brine produced and over half of the rock salt production. About three percent of the production is used as table salt, although more than this is utilized in the food processing industry.

#### Sodium Dichromate and Sodium Sulfate

Sodium dichromate ( $\text{Na}_2\text{Cr}_2\text{O}_7$ ) is prepared by the calcination of a mixture of chrome ore (typically chromite,  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ ), sodium



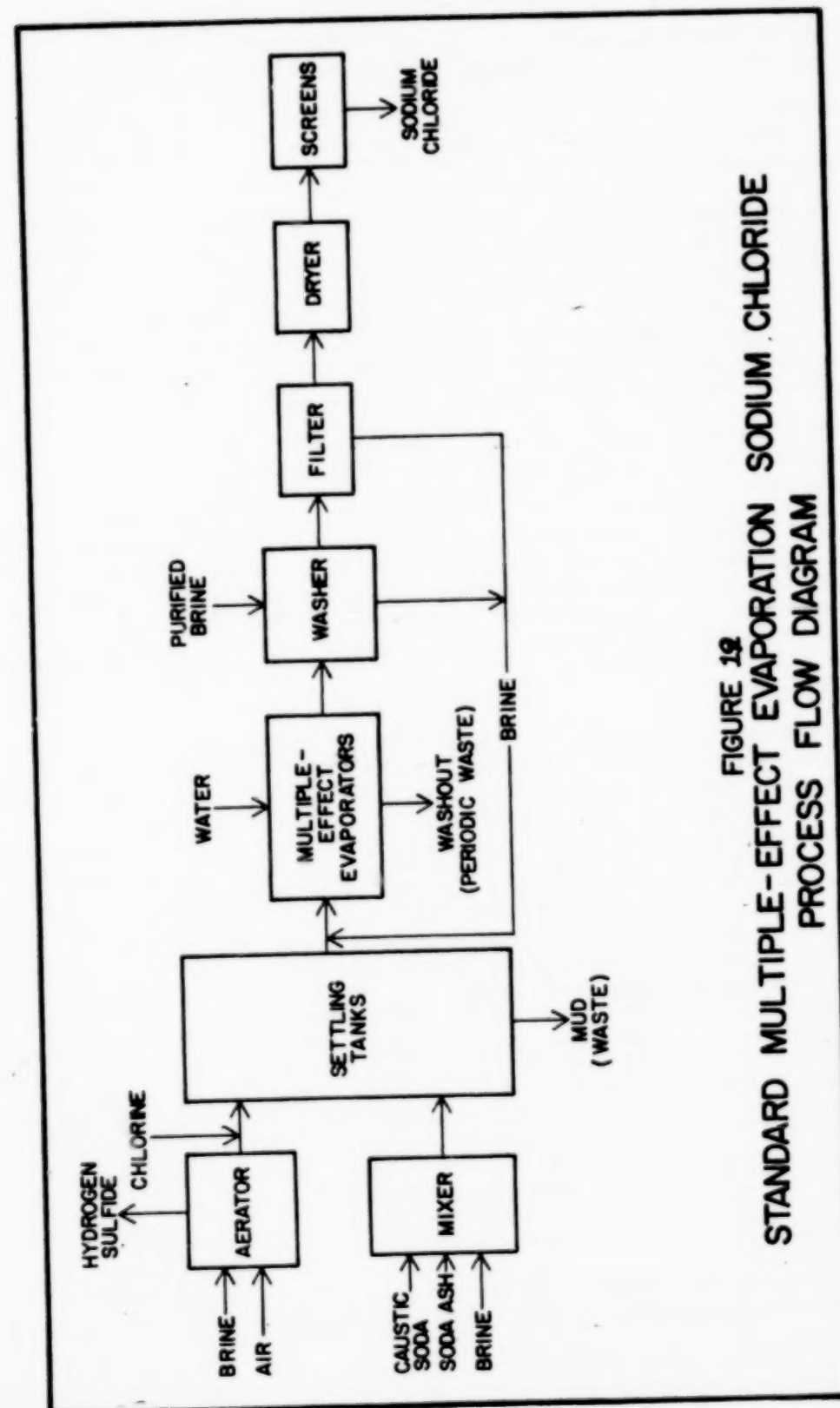
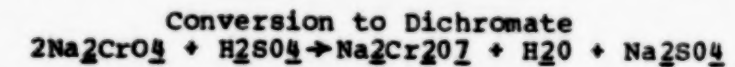
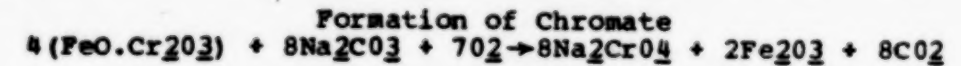


FIGURE 19  
STANDARD MULTIPLE-EFFECT EVAPORATION SODIUM CHLORIDE  
PROCESS FLOW DIAGRAM

carbonate, and lime. This is followed by a water leach and conversion of the soluble chromates to dichromate with sulfuric acid, as shown in Figure 20. The overall reaction scheme is:



After the leaching operation, calcium salts are precipitated by pH adjustment and then removed along with the iron oxide. The leachate containing the soluble chromate is then acidified by addition of sulfuric acid, thereby forming the dichromate and sodium sulfate. The sulfate is removed and the dichromate solution is partially evaporated and removed to a crystallizer where sodium dichromate crystals are allowed to form. The crystals are centrifuged to remove excess water and then dried and packed for shipment.

Other chromate products are often made in the same plant, including production of "chromic acid" (sold as the liquid solution of  $\text{CrO}_3$ ) by treatment of sodium dichromate with sulfuric acid, and sodium chromate, produced either by the chromite ore reaction above (crude chromate) or by reaction of sodium dichromate with soda ash (very pure product). Sodium dichromate is the major product of the industry. It is sold as an orange-colored dihydrate ( $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ ). Current production is estimated to be between 100,000 and 150,000 kkg (110,000 and 165,000 tons). The major demand for this chemical is in the manufacturing of pigments. Other uses include leather tanning, metal treatment, and corrosion inhibition.

Sodium sulfate (salt cake) is produced as a by-product from sodium dichromate manufacture, by direct mining and natural brine recovery operations, and as a by-product of organic syntheses. Most of the U.S. production arises from production of rayon and various organic chemicals and is not covered in this Document. Production from mining and natural brines is also not considered herein.

In sodium dichromate manufacture, soda ash, lime, and chrome ore are reacted as shown above. The products are then leached with sulfuric acid to convert the chromate to dichromate. The leachate, containing sodium sulfate in addition to sodium dichromate, is partially evaporated to the point where the sulfate is precipitated. The solid sulfate is filtered out, dried, and sold.

Since sodium sulfate is primarily a by-product material, the supply often exceeds the demand. In addition, the natural product is relatively abundant and limited in competition only by



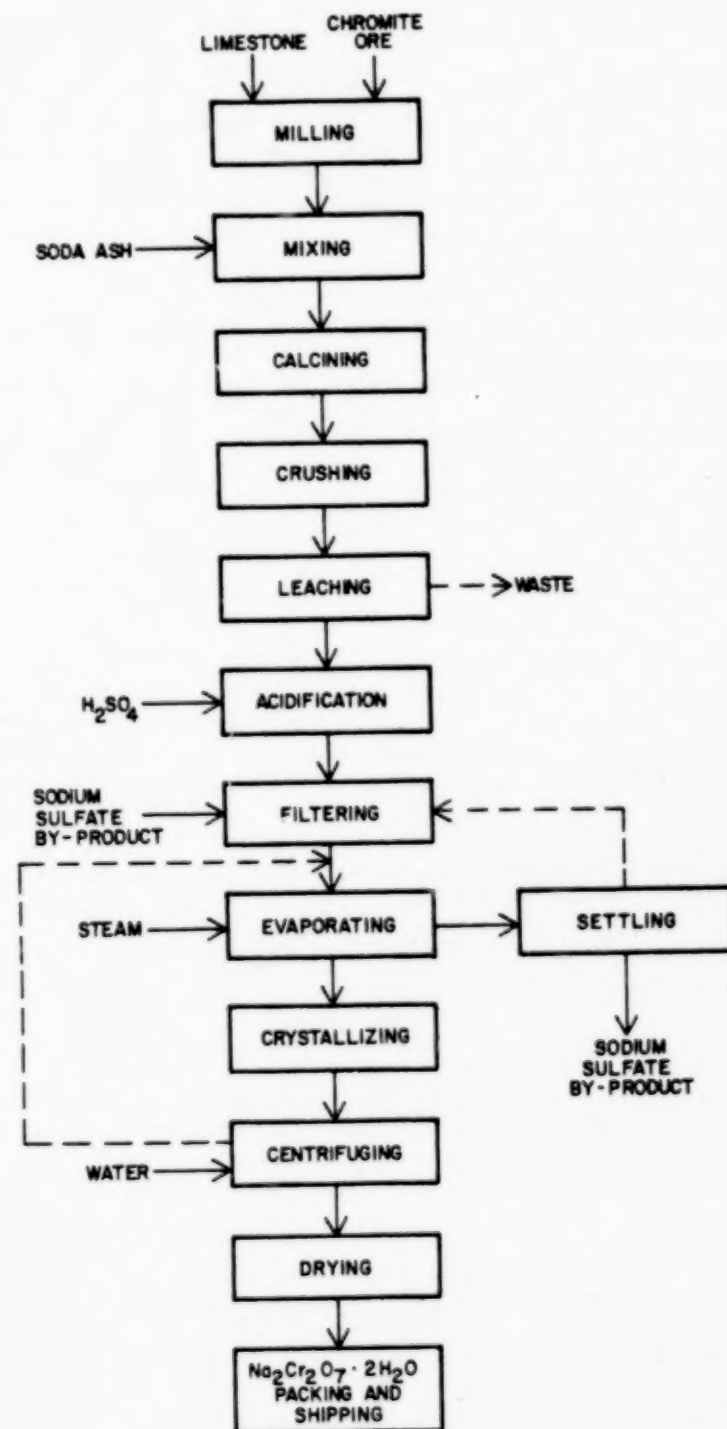
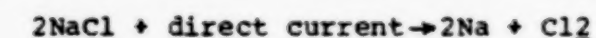


FIGURE 20  
STANDARD SODIUM DICHROMATE  
PROCESS DIAGRAM

distance from the markets. The largest use is in the kraft pulp and paper industry. Another major use is as a "builder" in detergents. Total U.S. production in 1971 was 764,409 kkg (842,788 tons) of high purity sodium sulfate and 465,785 kkg (513,545 tons) of Glauber's salt ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ). The dichromate by-product is sometimes called "chrome cake". Present annual production of this form of sodium sulfate is estimated to be 110,000 kkg (121,000 tons).

#### Sodium Metal

Sodium metal is manufactured by electrolysis of fused (molten) sodium chloride at about  $600^\circ\text{C}$  ( $1072^\circ\text{F}$ ), as shown in Figure 21. The general equation is:



After purification to remove magnesium salts and sulfates, the sodium chloride is mixed with alkali fluorides and calcium chloride to lower the melting point. The charge is then fused in a "Downs" cell, which is a closed rectangular refractory-lined steel box with separate anode and cathode compartments separated by an inorganic diaphragm. The graphite or carbon anode is fed into the bottom of the cell, and the cathode is iron or copper in an annular form.

Molten sodium formed at the cathode is transported to a collection vessel. The metal is withdrawn from the bottom, filtered, and packaged in the form of bricks of various sizes. Very pure metal results from blanketing the cell and other processing equipment with argon gas to prevent oxygen from entering the system. Even the less pure product, because of its reactivity, must be protected from air and water throughout the production process. By-product chlorine is liberated in the cell, dried with sulfuric acid and the purified product is compressed and sold.

The U.S. production of sodium metal in 1971 was 138,839 kkg (153,075 tons). One of its major uses is in the manufacturing of tetraethyl lead and other organometallic compounds. Other uses include production of sodium cyanide, sodium peroxide, titanium, and zirconium. It is also used in liquid form as a nuclear reactor coolant and as a light, thermally-conductive solid in various applications.

#### Sodium Silicate

Several forms of sodium silicate are manufactured including both liquid and anhydrous (solid or powder) forms of sodium metasilicate ( $\text{Na}_2\text{SiO}_3$ ), sodium orthosilicate ( $\text{Na}_4\text{SiO}_4$ ), and sodium tetrasilicate ( $\text{Na}_2\text{Si}_4\text{O}_9$ ). The liquid forms are generally sold in 20 - 50 percent by weight aqueous solutions called "water

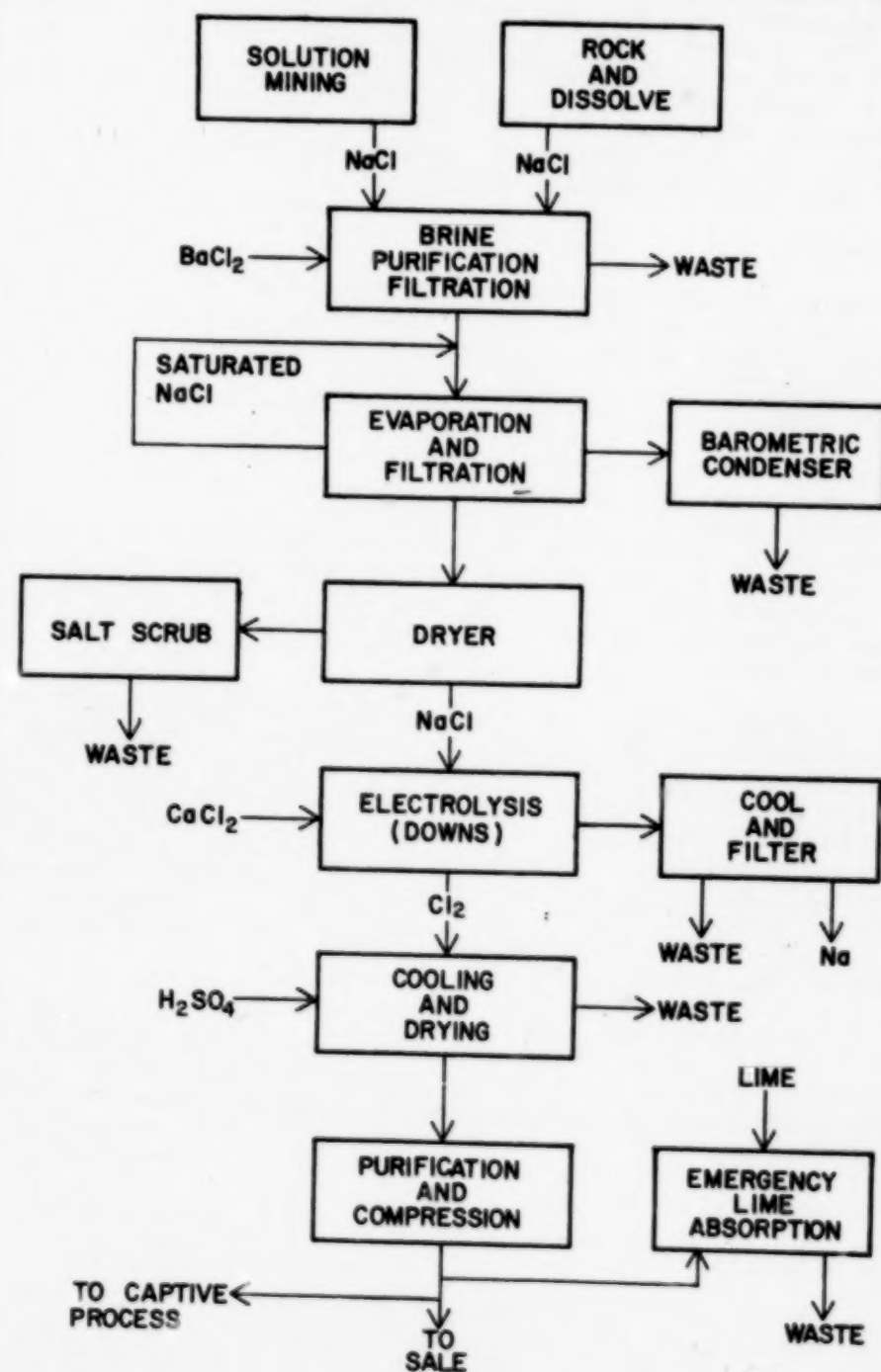
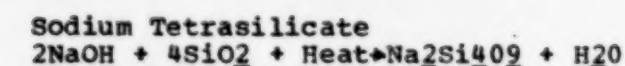
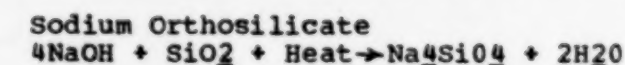
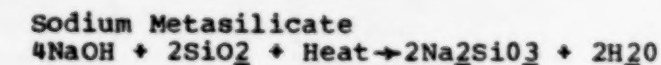


FIGURE 21  
STANDARD CHLORINE-SODIUM DOWNS CELL  
PROCESS FLOW DIAGRAM

glass", because they solidify to a glass which is water-soluble. The general production process as shown in Figures 22 and 23, involves reaction of caustic soda (NaOH) and silica (SiO<sub>2</sub>). The relative proportions of the reactants determine the product composition. Equations for the several reactions are:



Sodium silicates, other than those listed above, can be produced by further variation of the caustic-silica reactant ratios.

In a typical process, caustic soda and silica sand are mixed in the desired proportion and charged to a furnace. Water and steam are added to the product under pressure to completely dissolve the silicate. The liquid product is then stored or used to produce silicate in solid form. The production of solid silicate from silicate solution essentially involves evaporation of the water, although the silicate in solution may be further reacted with a caustic solution during the process if a higher sodium crude content is desired in the solid product. This is typically the case in the production of sodium metasilicate (anhydrous) from tetrasilicate water glass. The dried anhydrous silicate is screened and milled to achieve the desired particle sizes.

Silicate plants are often captive to soap or catalyst manufacturers or other users. One of the major uses is in the manufacture of silica gel. In 1971, the U.S. production of sodium silicate in water glass form was 569,701 kkg (628,116 tons), and that of anhydrous sodium metasilicate was 244,808 kkg (269,910 tons).

#### Sodium Sulfite

The major process for sodium sulfite manufacture consists essentially of reacting sulfur dioxide with soda ash (Na<sub>2</sub>CO<sub>3</sub>). Another source is as a by-product from the production of phenol through the reaction of sodium benzene sulfonate with sodium hydroxide. The latter is not considered in this Document.

In the soda ash-sulfur dioxide reaction process, shown in Figure 24, the sulfur dioxide gas is passed into a solution of sodium carbonate until the product is acidic. At this point the solute consists primarily of sodium bisulfite (NaHSO<sub>3</sub>), which is converted to sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>) by the further addition of

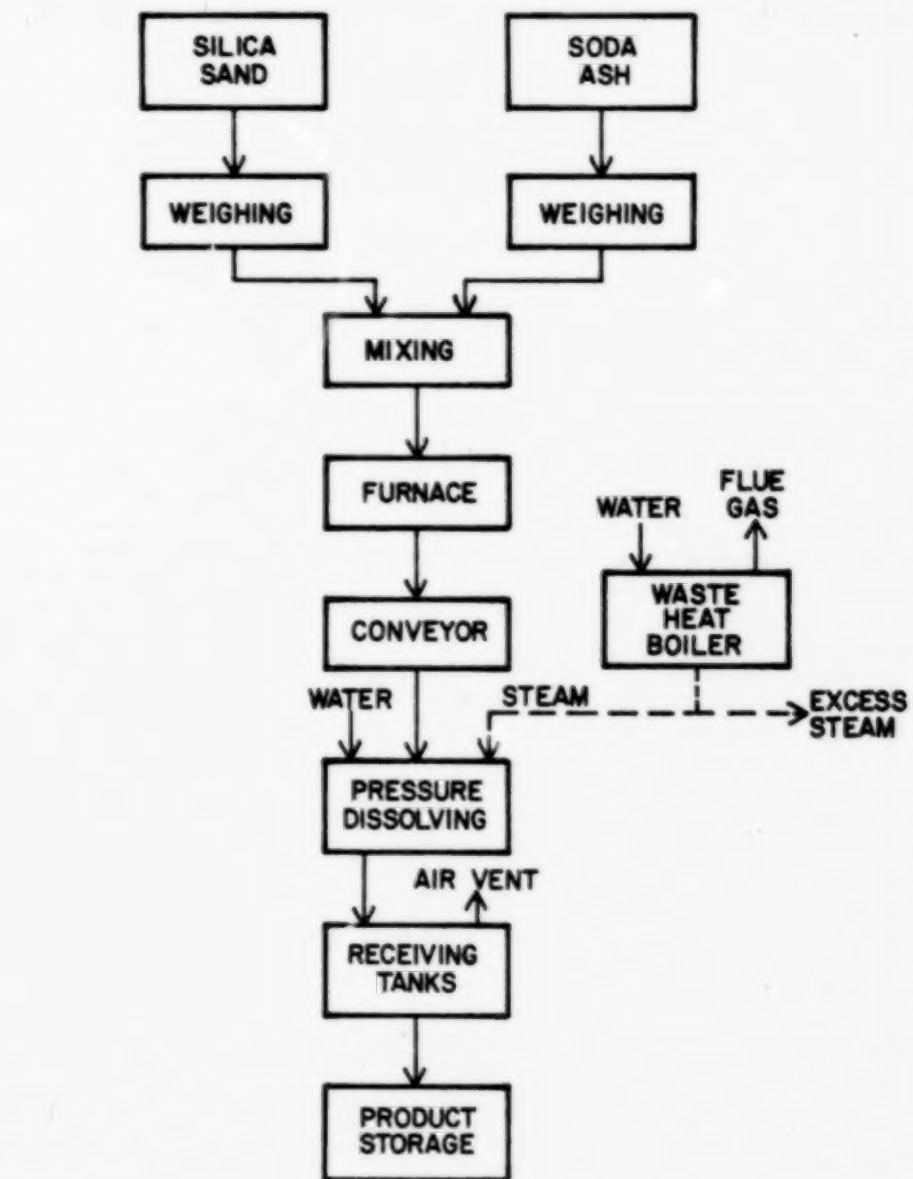


FIGURE 22  
STANDARD LIQUID SODIUM SILICATE  
FLOW DIAGRAM

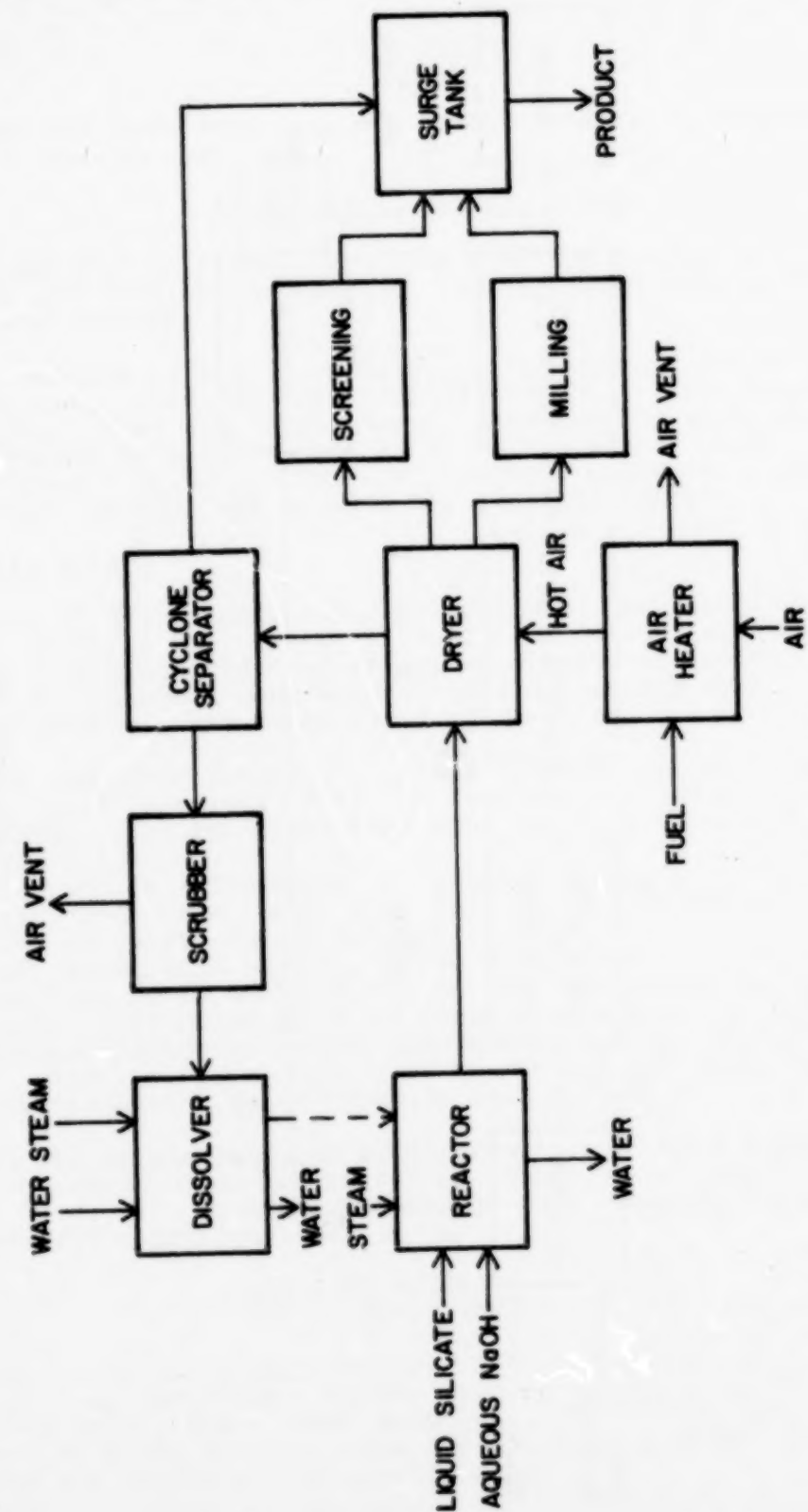


FIGURE 23  
STANDARD ANHYDROUS SODIUM METASILICATE  
FLOW DIAGRAM



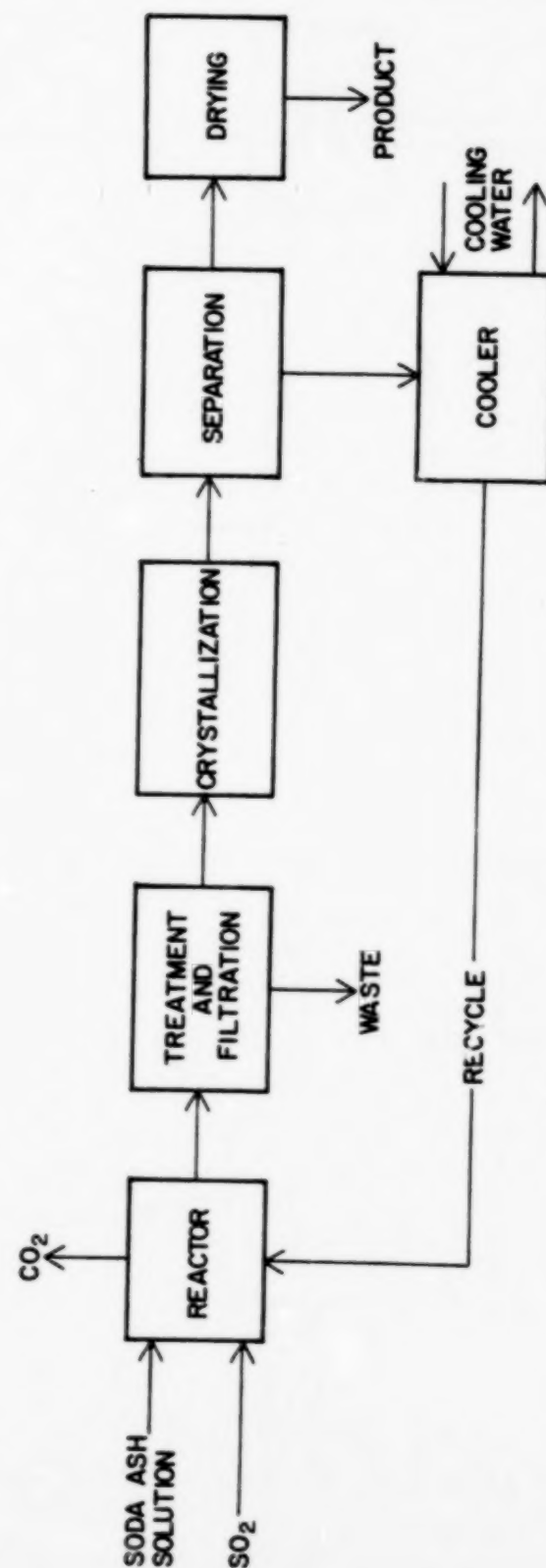
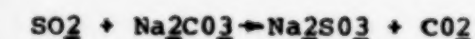


FIGURE 24  
STANDARD SODIUM SULFITE PROCESS FLOW DIAGRAM

soda ash and heat until all the carbon dioxide is released. The overall reaction is:



The crude sulfate formed from this reaction is purified, filtered to remove insolubles from the purification steps, crystallized, dried and shipped.

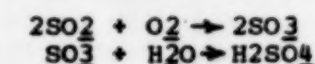
Sodium sulfite is a mild reducing agent, and is widely used as an antioxidant. Specific uses include bleaching and stabilization of yarns, textiles and paper, preservation of foodstuffs and photographic developers, and as a boiler feed water additive. The paper industry is the largest consumer. Total U.S. production in 1971 was 185,393 kkg (204,402 tons).

#### Sulfuric Acid

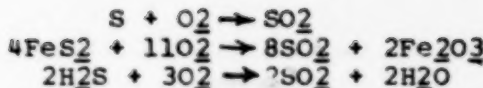
Sulfuric acid is manufactured primarily by the contact process, which involves the burning of sulfur to sulfur dioxide, followed by the catalytic oxidation of sulfur dioxide to sulfur trioxide which is reacted with water to yield sulfuric acid. Using the contact process, are three types of plants:

- (a) double absorption - paired sulfur trioxide absorption towers and catalyst beds in series are used to maximize conversion of sulfur dioxide so that tail gas scrubbers are not required;
- (b) single absorption - single absorption towers and catalyst beds are used and tail gases frequently have to be scrubbed to remove sulfur oxides;
- (c) spent acid plants - these plants use spent sulfuric acid in place of, or in addition to, sulfur as a raw material. While the acid production parts of these plants are the same as those for single absorption, these plants are unique because of the spent acid pyrolysis units used to convert the waste sulfur acid raw materials to a sulfur dioxide feed stream.

Almost all of the sulfuric acid production in this country arises from catalytic oxidation of sulfur dioxide to sulfur trioxide ( $\text{SO}_3$ ) and its subsequent reaction with water to form the acid. The general reactions are:



The source of the sulfur dioxide for acid manufacturing varies widely; raw materials include sulfur, refinery sludges, pyrites (sulfide ores), spent acid solutions, recovered  $\text{SO}_2$ , and by-product hydrogen sulfide. The sulfur, iron sulfide, and hydrogen sulfide are burned in air according to:



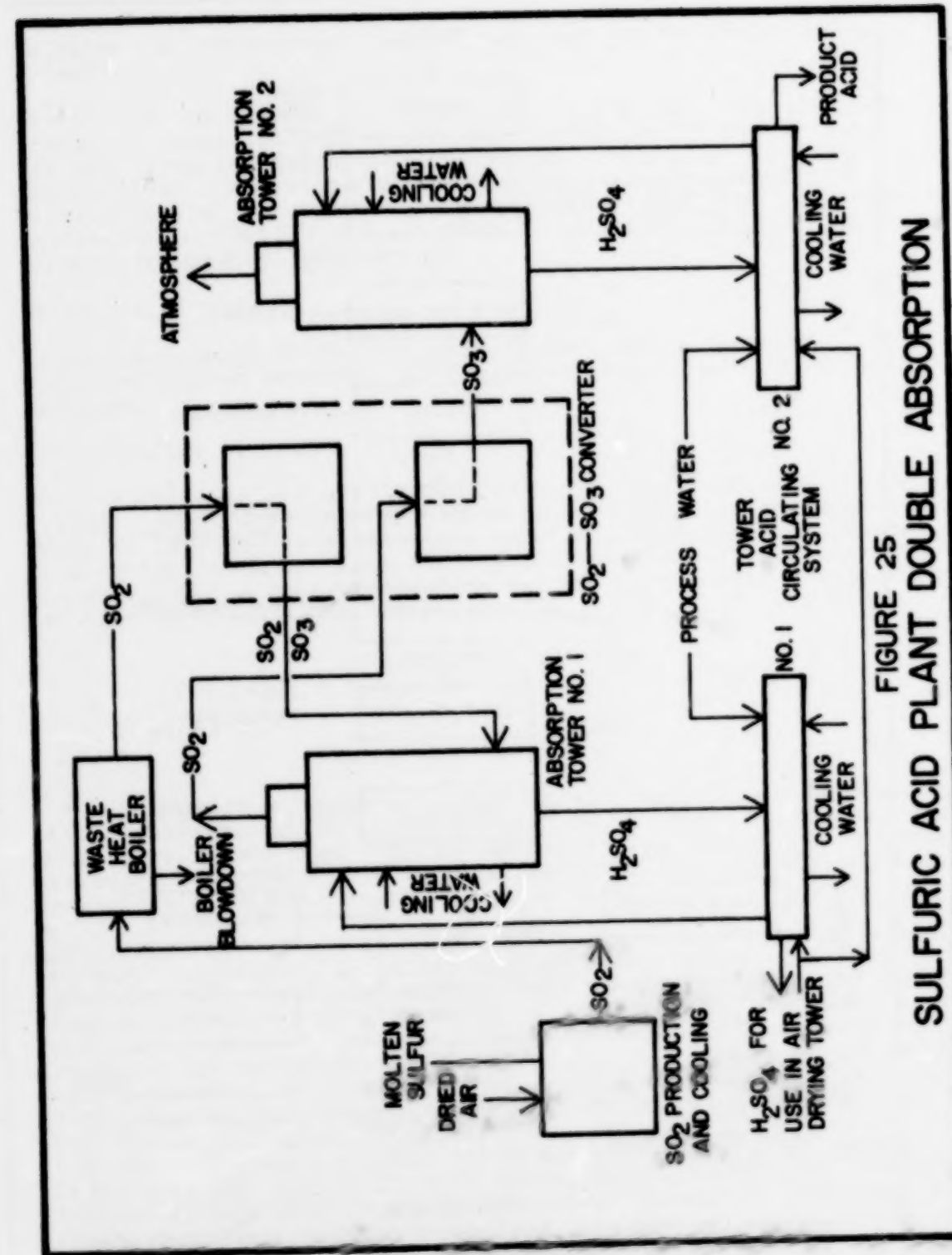
Sulfur dioxide from oxidation of iron sulfide or from roasting of other sulfide ores is relatively impure and requires removal of materials such as dust, moisture, arsenic, chlorine, and fluorine, all of which would poison the catalyst used in the contact process. Most of the U.S. production of sulfuric acid arises from the use of sulfur or refining sludge raw materials.

In the contact process, purified and dry sulfur dioxide is mixed with air, heated, and introduced into a reactor (converter) containing a platinum or vanadium pentoxide catalyst. The resulting gas mixture is cooled and sent to a succession of internally-cooled towers where the sulfur trioxide is absorbed by oleum (acid plus excess sulfur trioxide) of successively decreasing sulfur trioxide concentrations. Acid less than 97 percent concentration cannot be used to absorb sulfur trioxide because of mist formation and resulting sulfur trioxide losses. Various products are sold, ranging in acidic strength from battery acid (33.5 percent  $H_2SO_4$ , 50°Be) to 70 percent oleum (70 percent free  $SO_3$  in  $H_2SO_4$ ). Iron or steel containers can be used for the higher acid concentrations. Dilute acid requires specialized containers lined with glass, rubber, or lead.

In the double absorption contact process, sulfur is burned to yield dioxide which is then passed through a catalytic converter with air to produce sulfur trioxide. The sulfur trioxide is then absorbed in 95-97% sulfuric acid. The gases emerging from the absorber are then fed to a second converter to oxidize the remaining sulfur dioxide to sulfur trioxide which is then absorbed in a second absorption tower. The tail gases are vented to the atmosphere.

As in other versions of the contact process, 95-97 percent stream sulfuric acid is used in the absorption towers. Pickup of sulfur trioxide in this medium converts it to 98 percent acid. Some of this acid is drawn off for sale and the remainder is diluted back to 96-97 percent stream and recirculated through the absorption towers. A process flow diagram is given in Figure 25.

The single absorption process differs from that previously described only in the arrangement of the converters and absorbers. For the single absorption process, the sulfur dioxide is passed through one or more converters and then into one or more absorbers prior to venting to the atmosphere as shown in Figure 26. This arrangement is less effective for both conversion of sulfur dioxide to sulfur trioxide and for absorption of the sulfur trioxide into the absorber sulfuric acid. As a result, the tail gases may be scrubbed and this





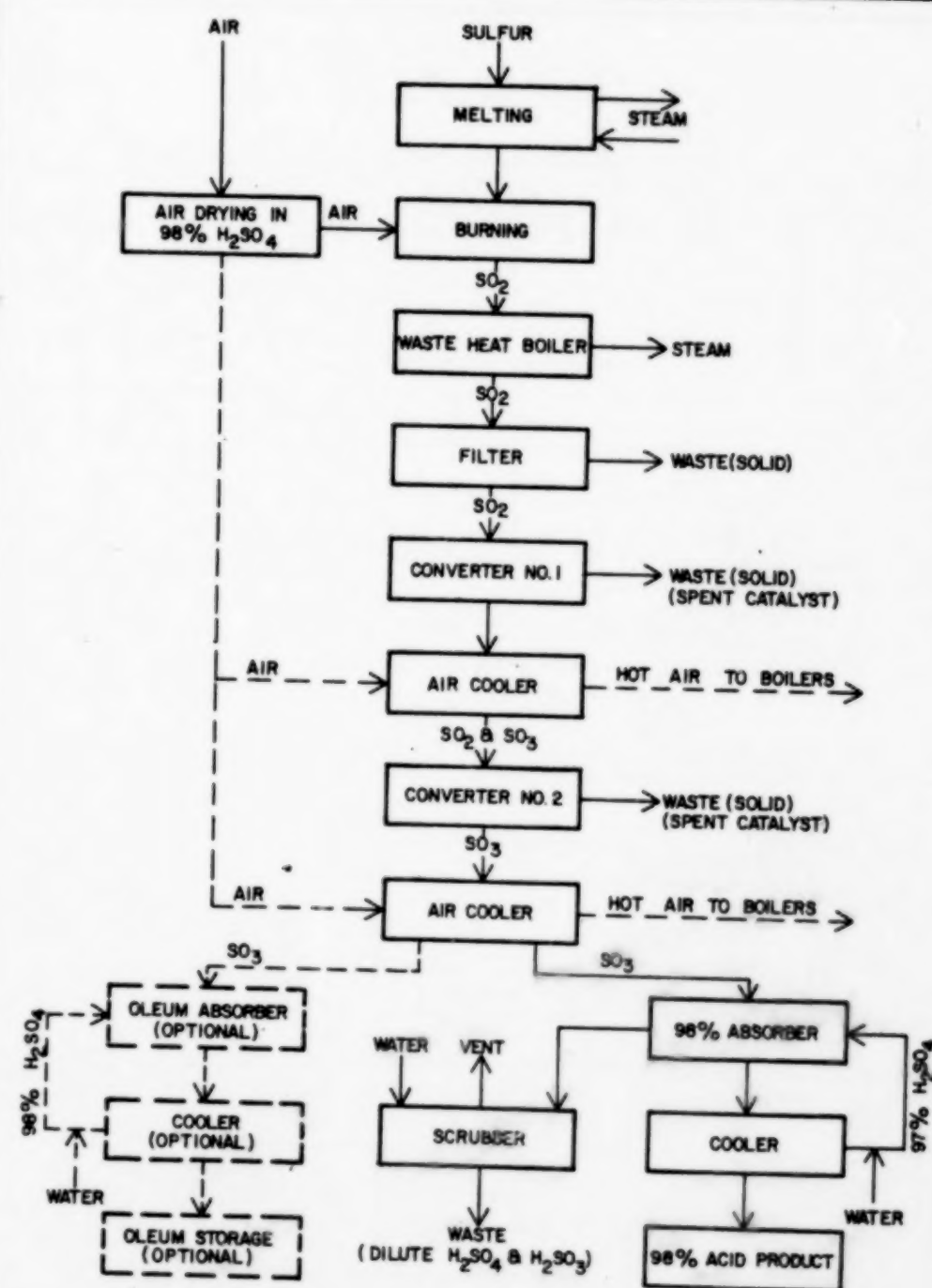


FIGURE 26  
STANDARD SULFURIC ACID SINGLE ABSORPTION  
FLOW DIAGRAM (CONTACT PROCESS)

creates a water-borne waste not present in double absorption plants.

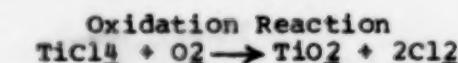
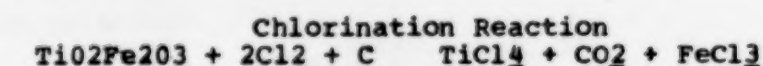
Total U.S. production in 1971 was 26,685,916 kkg (29,422,179 tons). About 60 percent of this production is captive, much of it supplying the fertilizer, petroleum refining, and explosive industries. There are many other large-tonnage industrial uses, including the manufacture of synthetic plastics, detergents, hydrofluoric acid, nuclear fuels, and various other organic and inorganic chemical products.

#### Titanium Dioxide

Titanium dioxide is the most widely used white pigment. It is produced by two methods, the "sulfate" process and the "chloride" process.

##### a) Chloride process

In the chloride process, shown in Figure 27, titanium dioxide ( $\text{TiO}_2$ ) ores are chlorinated to produce titanium tetrachloride. Coke is included to promote the reaction. The resulting titanium tetrachloride is oxidized to titanium dioxide and chlorine which is recycled. A general reaction scheme using rutile ( $\text{Fe}_2\text{O}_3 \cdot \text{TiO}_2$ ) as the raw material is shown below:



The chlorination reaction above is only approximate because the iron chloride which results may be a mixture of several chlorides, and some carbon monoxide is formed. The actual products and product ratios will depend on the composition of the raw material and the reactant ratios used.

Impurities in the system, including the iron and other metal (Al, V, etc.) chlorides, entrained coke and ore, carbon monoxide and dioxide, and hydrogen chloride all have to be removed prior to the oxidation reaction, creating a significant effluent waste control problem. After chlorination the products are cooled to condense the undesired metal chlorides. Solids are separated by centrifugation or filtration, and the gaseous titanium tetrachloride is condensed. Noncondensable reaction gases containing titanium tetrachloride, silicon tetrachloride and hydrogen chloride are water scrubbed, then vented. A number of techniques are used to further purify the tetrachloride, removing traces of silicon, vanadium, magnesium, manganese, aluminum, and chromium. These techniques include distillation, adsorption, ion exchange, and chemical precipitation with hydrogen sulfide,



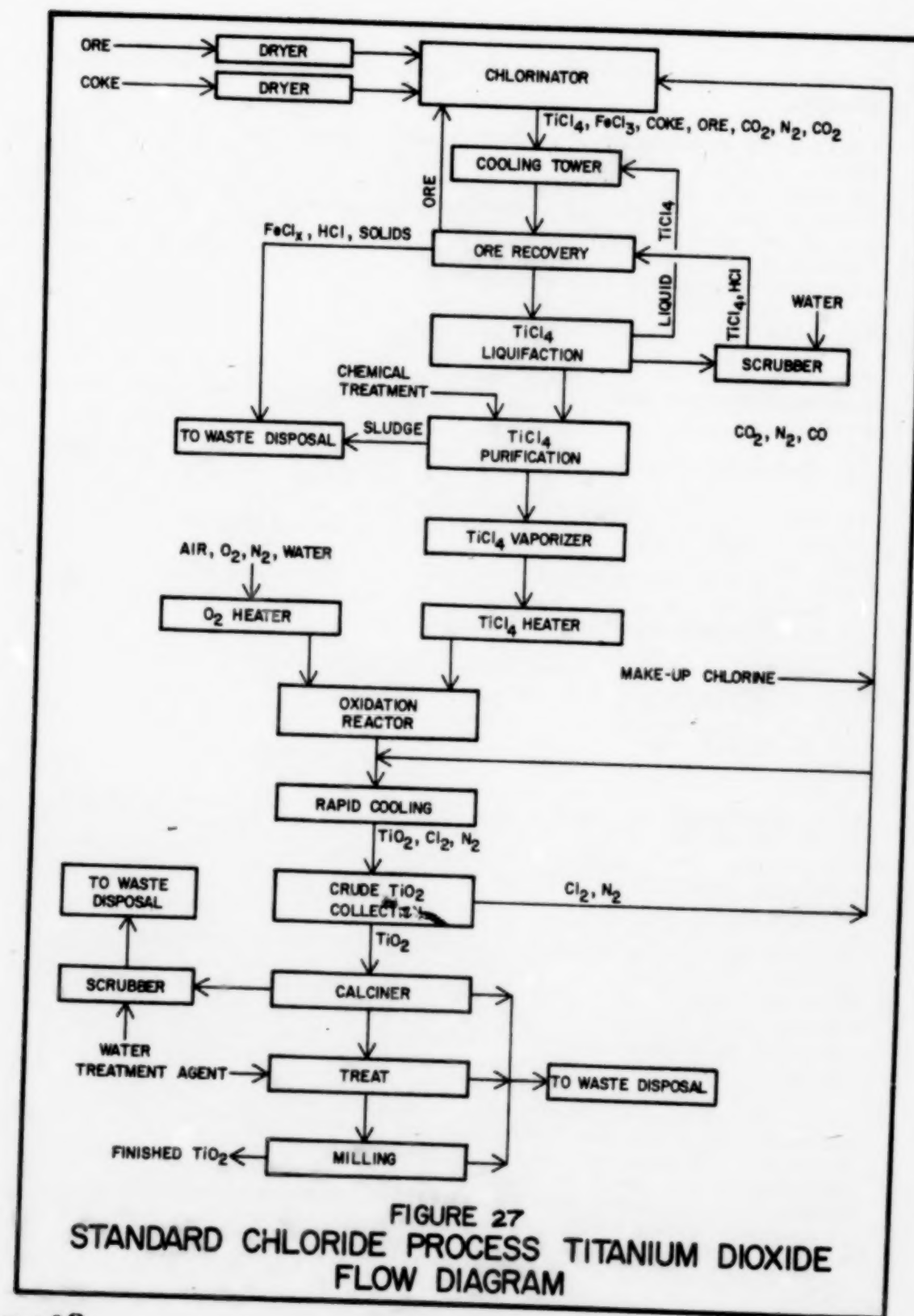


FIGURE 27  
STANDARD CHLORIDE PROCESS TITANIUM DIOXIDE  
FLOW DIAGRAM

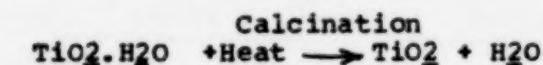
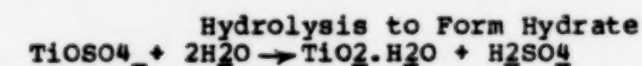
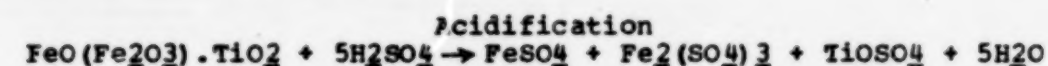
inorganic salts, or organic compounds. All techniques yield a pure titanium tetrachloride solution and a sludge which is slurried in water.

After purification, the titanium tetrachloride is vaporized and passed into a reactor with heated air or oxygen. The solid titanium dioxide particles are mechanically separated from the gas stream, calcined, ground, surface-treated, and packed.

#### b) Sulfate process

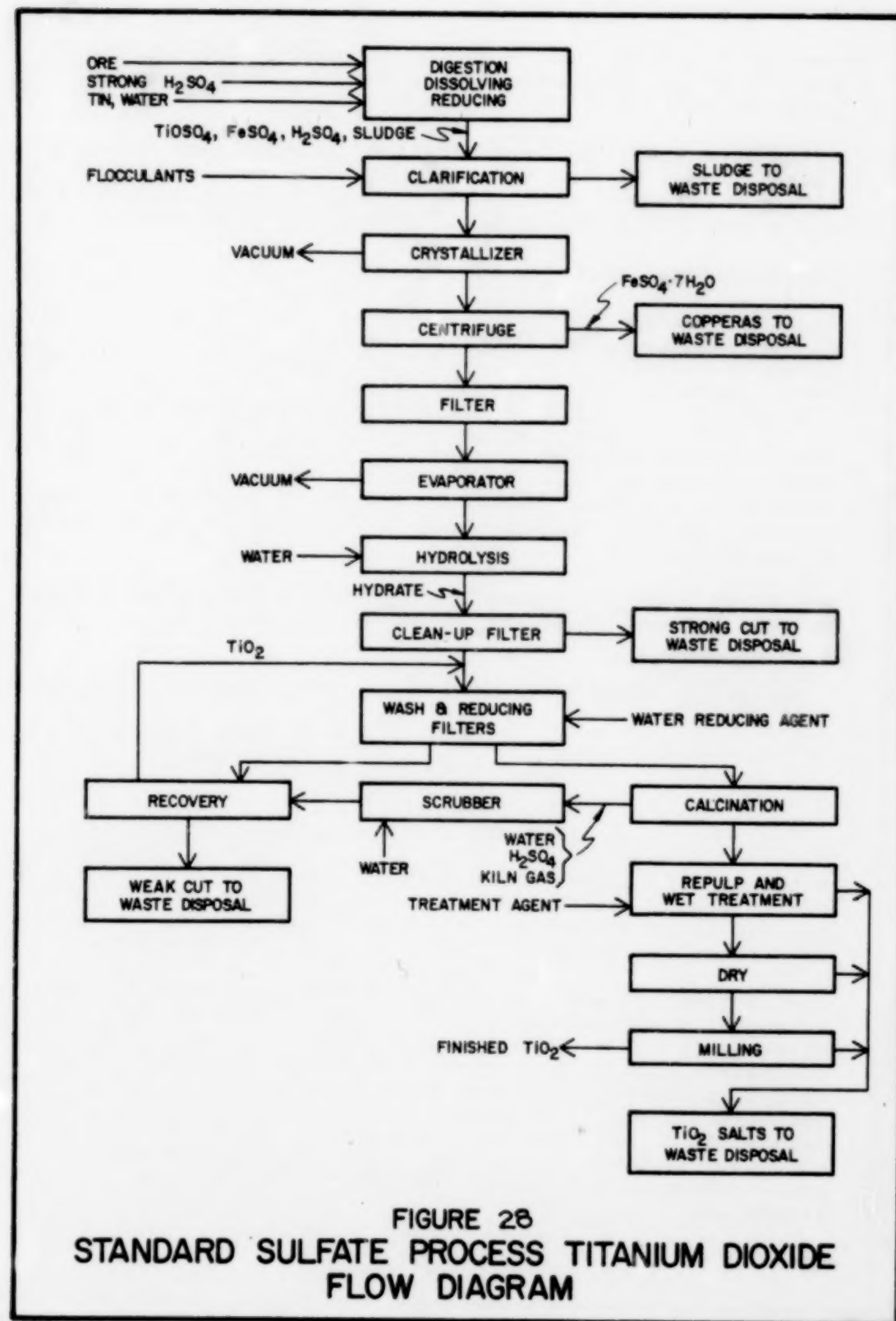
In the sulfate process, titanium dioxide-bearing ores are dissolved in sulfuric acid at high temperatures to produce titanium sulfate as an intermediate product. In some cases, small amounts of antimony trioxide are also added. The acid solution is clarified, a portion of the iron sulfates is removed by crystallization, and the titanium sulfate is hydrolyzed to form a white, non-pigmentary hydrate. The hydrate is calcined to form crystalline titanium dioxide, which is milled, surface treated, and packaged for sale. Product quality from the sulfate process is not so dependent on ore quality as is that from the chloride process.

A general reaction scheme using ilmenite containing various iron oxides (FeO and Fe2O3) is presented below:



After acidifications the solutions are clarified, cooled and sent to a vacuum crystallizer. There, ferrous sulfate crystallizes out and is separated from the mother liquor by centrifugation. This material is either sold or disposed of as a waste.

The mother liquor is clarified by filtration after addition of filter aids and further concentrated by vacuum evaporation. Seed crystals or other nucleating agents are added and the concentrated liquor is treated with steam to hydrolyze the titanyl sulfate present. This precipitates as acidic hydrated titanium. The precipitate is collected by filtration, washed several times and calcined at 900-950°C to yield titanium dioxide. This calcined product is ground, and further processed to yield a purer product. A standard process flow diagram is given in Figure 28.



Various grades, purities, and surface finishes of several crystalline forms are sold commercially. Although the paint industry is the major user, various types of titanium dioxide are used in paper, inks, fabrics, rubber, and floor coverings. Total U.S. production in 1971 was 614,720 kkg (677,751 tons). Domestic ore is found in New York and Florida, plus lesser amounts in North Carolina, Virginia, and Idaho. The remaining ore supply is imported, much of it from Canada and India. Most of the production of this pigment is captive to the large paint manufacturers.

SECTION IV  
INDUSTRY CATEGORIZATION

For the purpose of establishing effluent limitation guidelines for existing point sources and standards of performance for new sources, the inorganic chemicals manufacturing category has been segmented into subcategories based on the specific inorganic product manufactured. In cases where one chemical is produced by dissimilar processes, the product subcategory has been further subdivided. Although similar waste water constituents may be generated from various product groupings, as shown in Figure 29, and may be treated to similar concentrations, water requirements are specific for each chemical manufacturing process. Guidelines based on production volume must reflect this difference.

The separation of each product into individual subcategories simplifies the application of the effluent guidelines and standards of performance by providing unambiguous direction as to the application of a standard to a given point source. This is critical because of the great variety of product mix in existing facilities. The substantial advantage of clarity outweighs any technical advantages of product grouping.

In developing effluent limitations and standards of performance, it was necessary to examine numerous factors to determine whether additional segmentation of the industry is justified. The factors considered include:

- (a) Waste water constituents
- (b) Treatability of waste waters
- (c) Manufacturing process
- (d) Plant age
- (e) Plant size
- (f) Product mix
- (g) Raw materials
- (h) Air pollution control devices
- (i) Geographical location.

A summary of the rationale employed in determining whether these factors necessitate further subcategorization is presented below.

(a) Waste water constituents.

The selected subcategorization scheme reflects gross differences in the raw waste loads generated from different chemical manufacturing processes. While it is recognized that the character and quantities of waste water pollutants may vary within a product subcategory, this difference is not sufficient to justify additional segmentation. When two different processes



used to manufacture the same chemical generate dissimilar waste water constituents, they have been considered individually.

(b) Treatability of waste waters.

The treatability of waste water is determined largely by the volume of waste water and by the type of pollutants present. Thus, the above discussion on waste water constituents is applicable here.

(c) Manufacturing process.

Establishing subcategories based on product manufactured generally reflects differences between various manufacturing processes. The product subcategories are further segmented if two dissimilar manufacturing processes are commonly used.

(d) Plant age.

The relative age of plants within a product subcategory are determined by obsolescence due to process or equipment changes and not physical age. Hence, plant age is not an appropriate basis for subcategorization. No correlation between plant age and effluent quality is evident from plant data.

(e) Plant size.

Plant size generally has little effect on the quality of waste water generated from various chemical manufacturing processes. Although treatment costs per unit of production are somewhat lower when large quantities of water are treated, this difference is not sufficiently great to warrant further segmentation of the industry.

(f) Product mix.

Chemical plants vary greatly in terms of the number and types of products manufactured. More treatment options and a greater reuse potential exist in plants manufacturing many chemicals. However, treatment alternatives exist for small and single-product plants, such that additional subcategorization is unnecessary.

(g) Raw materials

Different raw materials are obviously used to manufacture different products. This difference is reflected in the selected subcategorization scheme. However, within a product subcategory raw materials of varying degrees of purity are used. Because ore beneficiation and cleaning may be used to treat impure ores, raw material quality does not justify further segmentation of the industry. In certain cases different raw materials do not alter

the treatability of the process effluent. This is demonstrated in aluminum sulfate production where bauxite or aluminum clays are used as the source of aluminum.

(h) Air pollution control devices.

The type of system used to control air pollution will have an effect on the water treatment requirements of a given plant. Wet scrubbing solutions are the only source of waste water in some chemical manufacturing processes. In general, scrubbing solutions may be treated and recycled or reused. In some cases, this solution may be sold as a weak product solution. Product recovery justifies conversion to a dry bag collection system for some manufacturing processes. Because of the options available to economically treat, sell, recycle, reuse or eliminate scrubbing solutions, it was considered unnecessary to subcategorize according to methods of air pollution control.

(i) Geographical location.

Geographical location is important in analyzing the feasibility of various treatment alternatives. Evaporation ponds are functional only in areas where net evaporation exceeds rainfall. Ocean dumping and deep-well disposal are possible only in certain areas, and must be consistent with local, State and Federal laws. The possibility of ground water contamination may preclude the use of unlined holding and settling ponds in many locations. The location of a plant, therefore, is an important factor in selecting the appropriate treatment technologies for a specific plant. Because alternative treatment systems are available to accommodate differences in climate, geology, etc., additional subcategorization based on plant location is not justified. Allowances have been provided to permit discharges from impoundment in locations where rainfall exceeds evaporation.

The product subcategories are shown below with process subdivisions where required:

- Aluminum chloride
- Aluminum sulfate
- Calcium carbide
- Calcium chloride
- Calcium oxide and calcium hydroxide
- Chlorine and sodium or potassium hydroxide
  - a. mercury cell process
  - b. diaphragm cell process
- Hydrochloric acid
- Hydrofluoric acid
- Hydrogen peroxide
  - a. electrolytic process
  - b. organic process
- Nitric acid

Potassium metal  
 Potassium dichromate and potassium sulfate  
 Sodium bicarbonate  
 Sodium carbonate  
 Sodium chloride  
     a. brine-mining process  
     b. solar evaporation process  
 Sodium dichromate and sodium sulfate  
 Sodium metal  
 Sodium silicate  
 Sodium sulfite  
 Sulfuric acid  
 Titanium dioxide  
     a. chloride process  
     b. sulfate process.

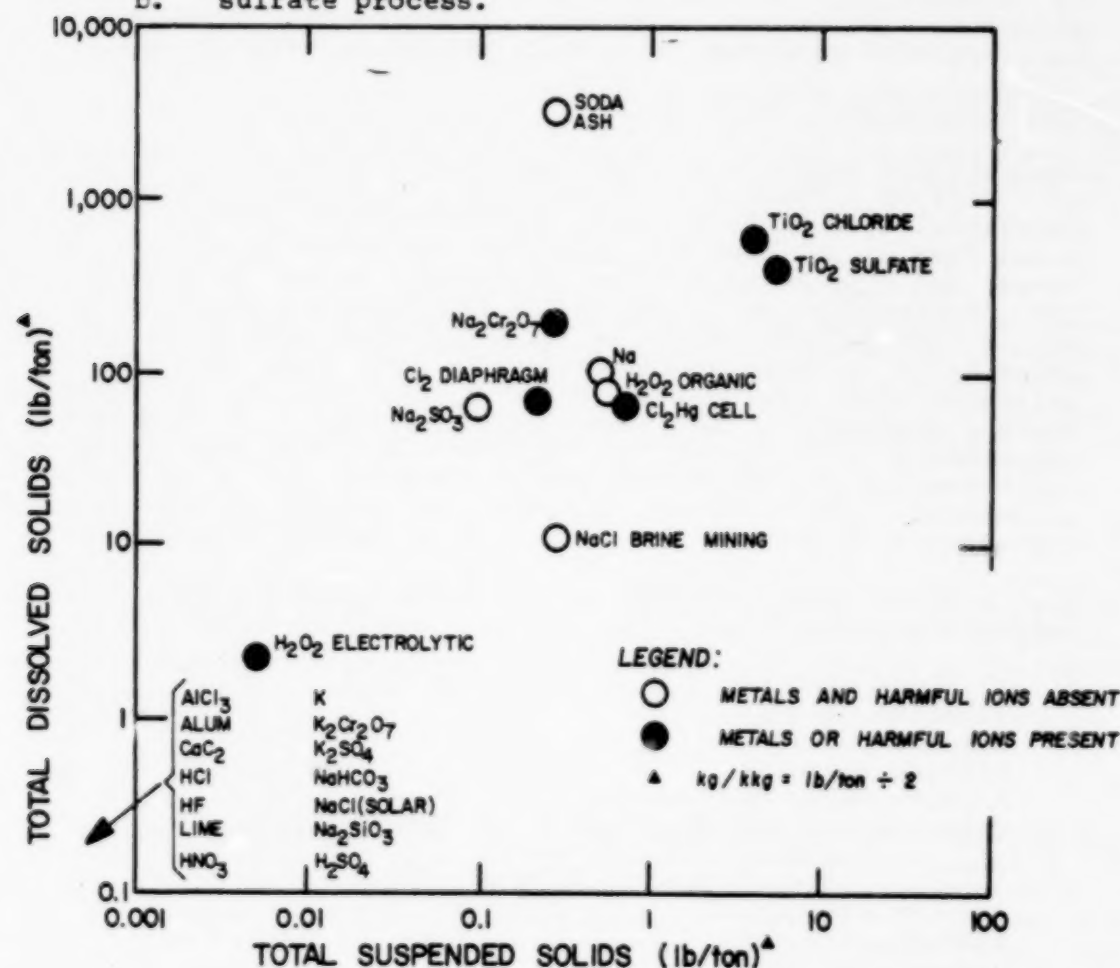


FIGURE 29  
 INDUSTRY CATEGORIZATION OF  
 INORGANIC CHEMICALS MANUFACTURING

## SECTION V

### WATER USE AND WASTE CHARACTERIZATION

This section discusses the specific water uses required in the manufacturing processes for the inorganic chemicals studied, and the amounts of waste effluents contained in these waters. The process wastes are characterized as raw waste loads emanating from a typical process before treatment and the amount of water-borne waste effluent after treatment. Also included in this discussion are verification sampling data measured at specific plants for each of the chemical subcategories set forth in Section IV. A description of the analytical techniques used for this verification of plant data is also provided.

#### GENERAL WATER USES

Water is used in inorganic chemical manufacturing plants for six principal purposes, plus other miscellaneous uses. The principal uses are:

- 1) Cooling -- Non-contact cooling water
- 2) Process -- Contact cooling or heating water  
                   Contact wash water  
                   Transport water  
                   Product and dilution water
- 3) Auxiliary water

The effluent guidelines developed in the document are to be applied to process waste water pollutants only. This includes those waste water constituents in water which directly contacts the product, by product, intermediate, raw material, or waste product. The guidelines do not include noncontact cooling water, or wastes resulting from steam or water supply. Guidelines for these waste streams will be developed in a separate study at a later date.

#### Non-Contact Cooling Water

Many chemical processes operate more quickly or more efficiently at high temperatures or generate heat. Cooling water is often used to control or reduce these temperatures. If the water is used without contacting the reactants, such as in a tube-in-shell heat exchanger or trombone cooler, then the water will not be contaminated with process effluent. If, however, the water contacts the reactants, then contamination of the water results and the waste load increases.

The non-contact cooling water in the industry is of two types. The first type is recycled cooling water which is cooled by cooling towers or spray ponds. The second type is once-through



cooling water whose source is generally a river, lake or tidal estuary, and this water is usually returned to its source.

The only waste effluent from recycled water would be water treatment chemicals and the cooling tower blowdown which generally is discharged with the cooling water. The only waste effluent from the once-through cooling water would be water treatment chemicals which are generally discharged with the cooling water. The cooling water tower blowdown may contain phosphates, nitrates, nitrites, sulfates and chromates. The water treatment chemicals may consist of alum, hydrated lime, or alkali metal ions (sodium or potassium) arising from ion exchange processes. Regeneration of the ion exchange units is generally accomplished with sodium chloride or sulfuric acid, depending upon the type of unit employed.

#### Contact Cooling or Heating Water

This water comes under the general heading of process water because it comes into direct contact with process reactants. This type of water is used by steam drum dryers and barometric condensers. Water is required in very large quantities for use in the barometric condensers used to provide reduced pressure for the operation of multiple effect evaporators. For a large triple-effect evaporator, such as that used for salt evaporation, flows of 3,800-41,600 cu m/day (1 to 11 million gallons per day) are not unusual. A waste effluent problem with the barometric condenser usage arises from the product vapors and carry-over from the last effect (stage) of the evaporator which are entrapped in the flow of condenser water.

Other direct contact cooling or heating water usage such as that for contact steam drying, steam distillation, pump and furnace seals, etc., is generally of much lower volume than the barometric condenser water.

#### Contact Wash Water

This water is considered process water because it comes into direct contact with either the raw material, reactants or products. Examples of this type of water usage are ore washing to remove fines, filter cake washing to remove entrained particles, cleansing of insoluble product vapors, and absorption processes wherein water is reacted with a gaseous material to produce an aqueous solution.

#### Transport Water

Water is often used in the inorganic chemicals manufacturing industry for transporting reactants or products to various unit operations either in solution, suspension or slurry form. A good example of this is solution-mined salt or brine. Water is pumped

into a salt cavity at the rate of 3900 l/kg (936 gal/ton) of salt. The salt is dissolved, and the resulting brine is forced to the surface under pressure where it can be fed to evaporators to produce dry salt, or fed to electrolytic cells where it is used to produce chlorine and alkali. Wastes resulting from these types of operations are generally dilute solutions or suspensions which could be reused upon concentration or could be returned to the source. In cases where transport water is carrying a solid product, it normally is separated from the product by filtration, evaporation, or drying. The resultant liquor or condensate generally contains dissolved product, reactants or impurities.

#### Product Water

The product water generally is that which comes in contact with and becomes an integral part of the product. Typical examples include digestion water used for sodium silicate manufacture and water used in acid absorption towers. Likewise, water may be added to a highly concentrated product to form a more dilute product. The source of these waters is generally fresh water supplies, steam condensate, dilute product streams, or a combination of these sources.

#### Auxiliary Process Water

This water is used for auxiliary operations such as ion exchange regenerants, make-up water to cooling towers with a resultant cooling tower blowdown, make-up water to boilers with a resultant boiler blowdown, and storage and shipping tank washing. The water effluents from these operations are generally low in quantity but highly concentrated in waste materials.

#### Miscellaneous Water Uses

These water uses vary widely among the plants with general usage for floor washing and cleanup, safety showers and eye wash stations, sanitary uses, and storm run-off. The resultant streams are either not contaminated or only slightly contaminated with wastes. In instances where process residues collect where they can be washed away by storm waters, as for example, dusts on the exterior of process buildings, storm run-off can constitute a serious contamination problem.



PROCESS WASTE CHARACTERIZATION

Aluminum Chloride

Aluminum chloride is made by reaction of chlorine with molten aluminum. The aluminum chloride formed vaporizes and is collected on air cooled condensers. The tail gases leaving the condensers are the only source of wastes downstream of the reaction zone. Plant 125 is the exemplary plant for this production process. Figure 30 shows a scrubber system for this plant.

In the process described above, there are two sources of waste-uncondensed aluminum chloride and chlorine in tail gases and unreacted aluminum metal. At the exemplary facility, the first waste is utilized to manufacture another product and the unreacted aluminum is disposed of as a solid waste.

The raw waste loads are shown below:

Waste Product	Source	kg/kg of Product (lb/ton)	
		Average	Range
AlCl <sub>3</sub>	Tail Gases	80 (160)	64-96 (128-192)
Unreacted Aluminum	Reactor	22 (44)	

At the exemplary plant there is an integrated blower system to exhaust the plant, packing station, condensers, etc. All blower exhaust is treated in an absorption tower where, as shown in Figure 30, the aluminum chloride and chlorine vapors are absorbed into a recycling scrubber system. From this scrubber, about 121 l of solution/kg of product (29 gal/ton) are drawn off, filtered and further treated to produce a 28 percent aluminum chloride solution which is sold. There are no waste streams. The water input and use for the scrubber system is an equivalent volume. This water is supplied from a well for makeup to the system. None of this is recycled. It is used to make 28 percent solution product.

The characteristics of the 28 percent aluminum chloride solution recovered for sale are tabulated below:

Aluminum Chloride Solution	
ACS-0002	
Technical Grade	
AlCl <sub>3</sub> percent	28 min.
Baume' at 15°C	32° min.
Total aluminum as aluminum oxide, percent	10.5 min.
Color, APHA	100 max.
Free Aluminum, percent	0.1 max.
Fe	25 mg/l

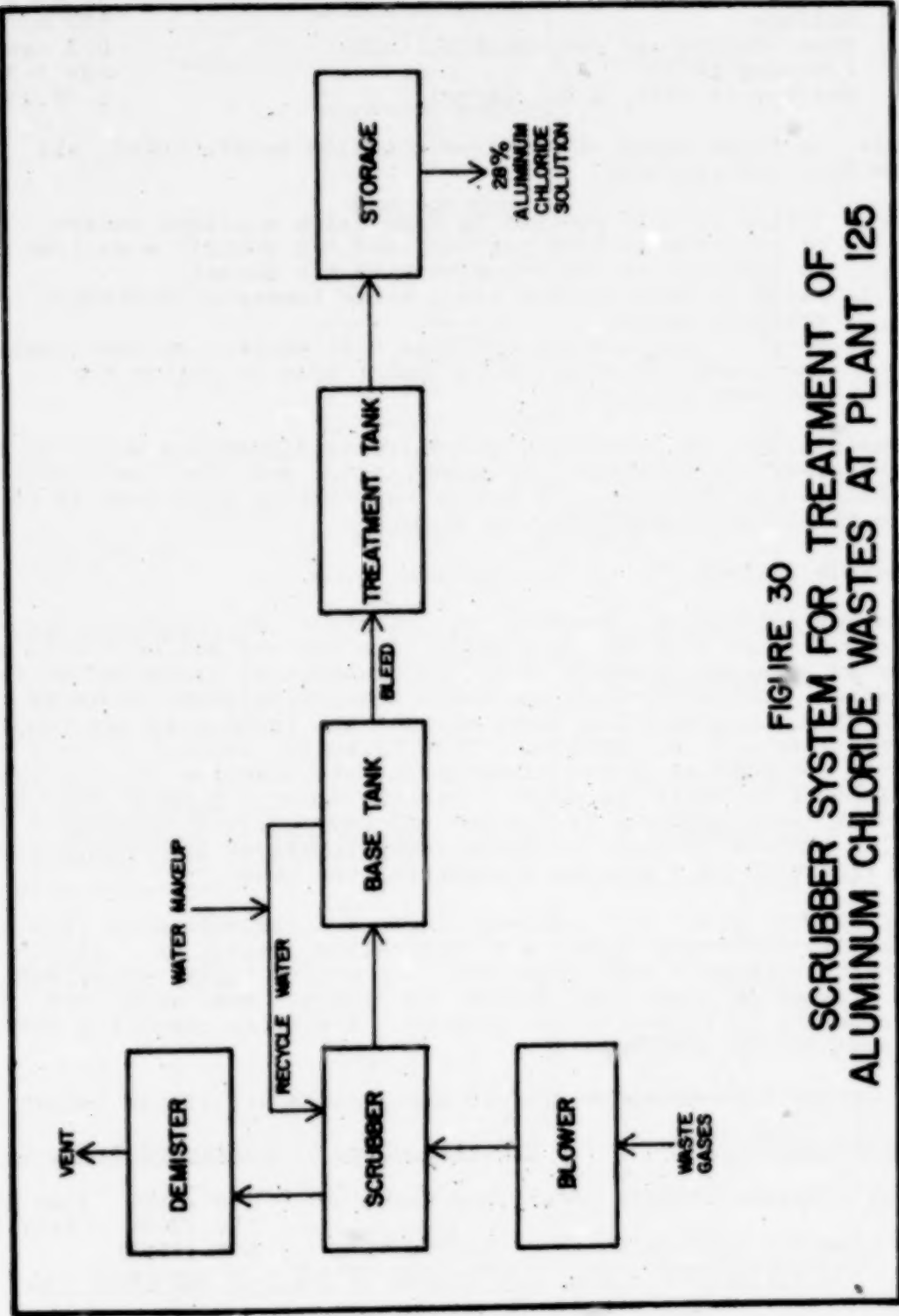


FIGURE 30  
SCRUBBER SYSTEM FOR TREATMENT OF  
ALUMINUM CHLORIDE WASTES AT PLANT 125

Heavy metals	10 mg/l
Sulfate	500 mg/l
Free Acidity as percent <sup>®</sup> HCl	0.2 max.
Freezing point	-34 (-30)
Density at 15°C, g/cc (lb/gal)	1.28 (10.7)

There are three types of aluminum chloride manufactured, all from the same process:

1. Yellow -- this product is made using a slight excess of chloride (0.0005 percent) and may contain some iron due to reaction of the chlorine with the vessel.
2. White -- this product has a stoichiometric aluminum/chloride ratio.
3. Grey -- this product contains 0.01 percent excess aluminum. The unreacted aluminum raw waste load is higher for the grey material.

Industrially, it generally makes little difference which of the above grades is employed. In some pigment and dye intermediate applications, however, the yellow material is preferred as it is free of elemental aluminum.

#### Aluminum Sulfate

Aluminum sulfate is prepared by reaction of bauxite ore or aluminum clays with sulfuric acid. The ore and sulfuric acid are reacted in a digester and the resulting aluminum sulfate solution, containing muds and other insolubles from the ore, is then fed to a settling tank, wherein the insolubles are removed by settling and filtration. The filtered product liquor is either shipped as liquid aluminum sulfate solution or evaporated to recover a solid product. Two exemplary plants for this product were studied, plants 049 and 063. Figure 31 shows a detailed process diagram including waste treatment for one plant, and Figure 32 is a similar diagram for the other.

Raw wastes from the process include insoluble muds from the digester, settling tank and filtration unit, as well as washwaters from vessel cleanouts. At one facility, these wastes are treated in a settling basin to remove the muds and the supernatant is reused in the process. A similar recycling system is used in the other facility.

Raw wastes from aluminum sulfate manufacture are listed below:

Waste Products	Process Source	kg/kg of Product (lb/ton)
Spent aluminum sulfate muds	Mud washing	170 (340) (two different facilities)
Low aluminum sulfate water	Mud washing	800 (1600)

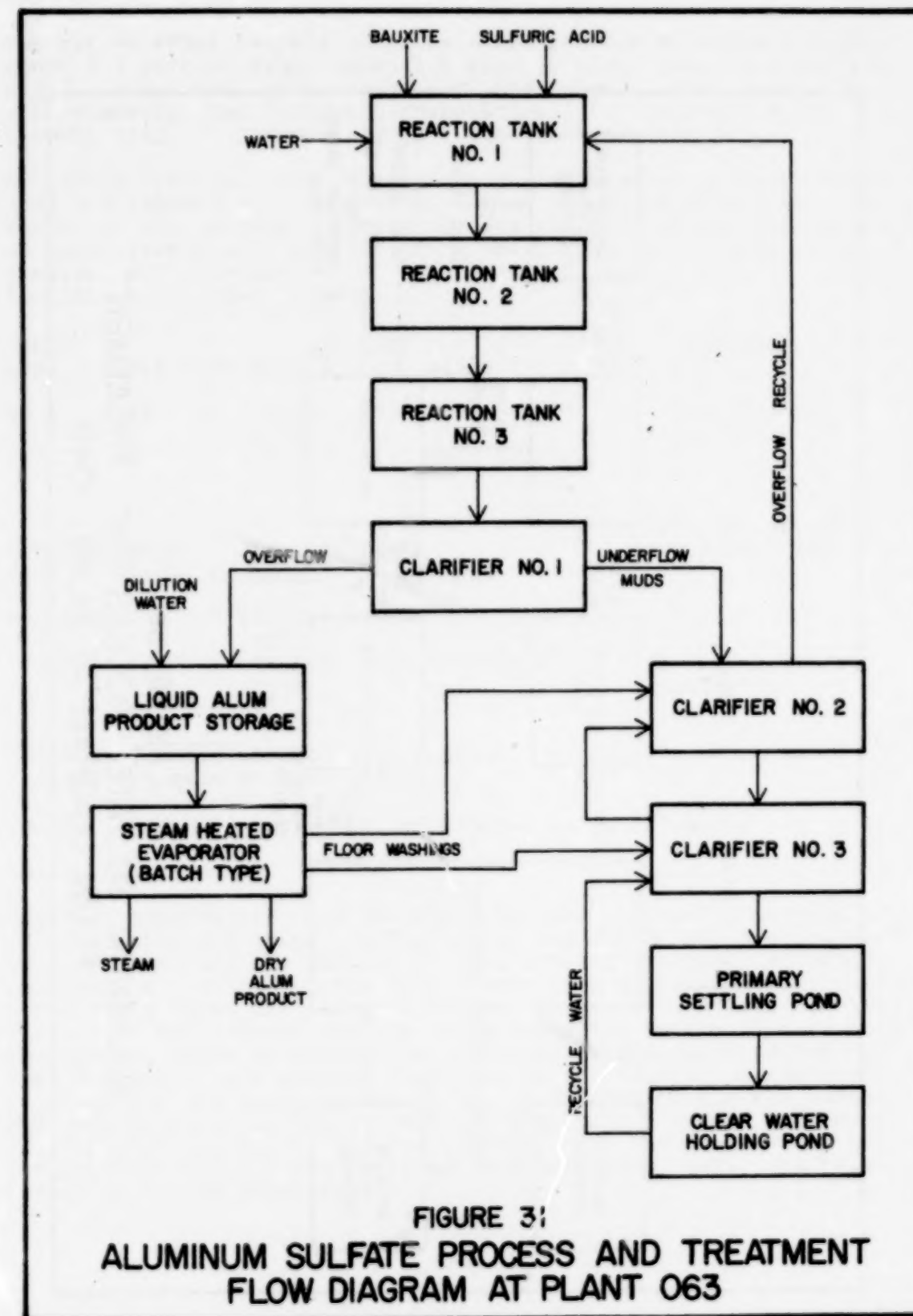
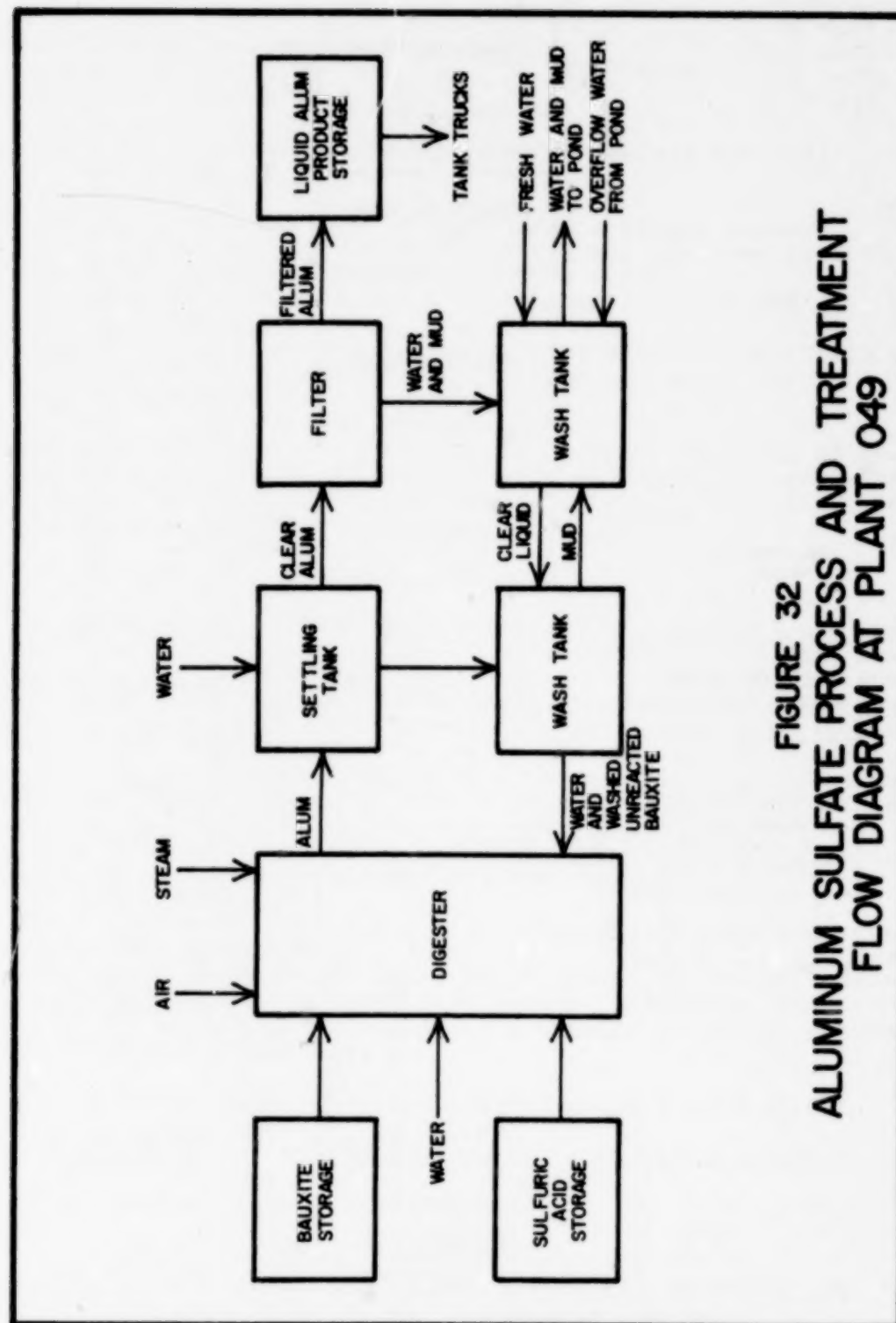


FIGURE 31  
ALUMINUM SULFATE PROCESS AND TREATMENT  
FLOW DIAGRAM AT PLANT 063



The raw material bauxite contains 54-56 percent of soluble  $\text{Al}_2\text{O}_3$ , about 3.5 percent  $\text{TiO}_2$ , about 5.5 percent  $\text{SiO}_2$ , about 1.5 percent  $\text{Fe}_2\text{O}_3$  and the rest water of hydration. The muds have, approximately, the following compositions: 40 percent  $\text{SiO}_2$ , 40 percent  $\text{TiO}_2$ , 20 percent  $\text{Al}_2\text{O}_3$ , 0.5 percent  $\text{Al}_2(\text{SO}_4)_3$ .

At these plants, all waters are fed to a settling basin where muds are removed and impounded. The clear effluent is then reused in the process. Provisions are established for collection of all leaks and spills which are pumped to the impoundment, treated and recycled. A breakdown of water use at both facilities is shown below:

<u>Input</u> <u>Type</u>	<u>Plant</u>	<u>cu m/day</u>	<u>Quantity</u> <u>l/kgq</u>	<u>Comments</u>
Well	049	47 (12,400 gpd)	1650 (396 gal/ton)	No Pretreatment Required for
Well	063	76 (20,000 gpd)	2090 (500 gal/ton)	Either
				Percent of Process Stream Recycled
<u>Process</u> <u>Type</u>	<u>Water</u> <u>Plant</u>	<u>cu m/day</u>	<u>Quantity</u> <u>l/kgq</u>	
Process	049	77 (20,400 gpd)	2720 (652 gal/ton)	30*
Process	063	87 (23,000 gpd)	2400 (575 gal/ton)	All excess process water*

\*Remaining water shipped with product. Aluminum sulfate solutions are made at both plants.

These plants have no process or cooling water effluent.

### Calcium Carbide

Calcium carbide is manufactured by the thermal reaction of calcium oxide and coke. Calcium oxide and dried coke are reacted in a furnace, and the product is then cooled, crushed, screened, packaged and shipped. The only wastes from the process are airborne dusts from the furnace, coke dryer and screening bag filters. Bag filters are now being installed in the furnace and the packing areas of plant 190. All collections are returned to the furnace. The process locations of the sources of raw waste in plant 190 are shown in Figure 33. A listing of the raw wastes and amounts is given below. All but the cooling tower blowdowns are treated by dry collection methods. The blowdown wastes are intermittent and are currently untreated. This data was furnished by the manufacturer.



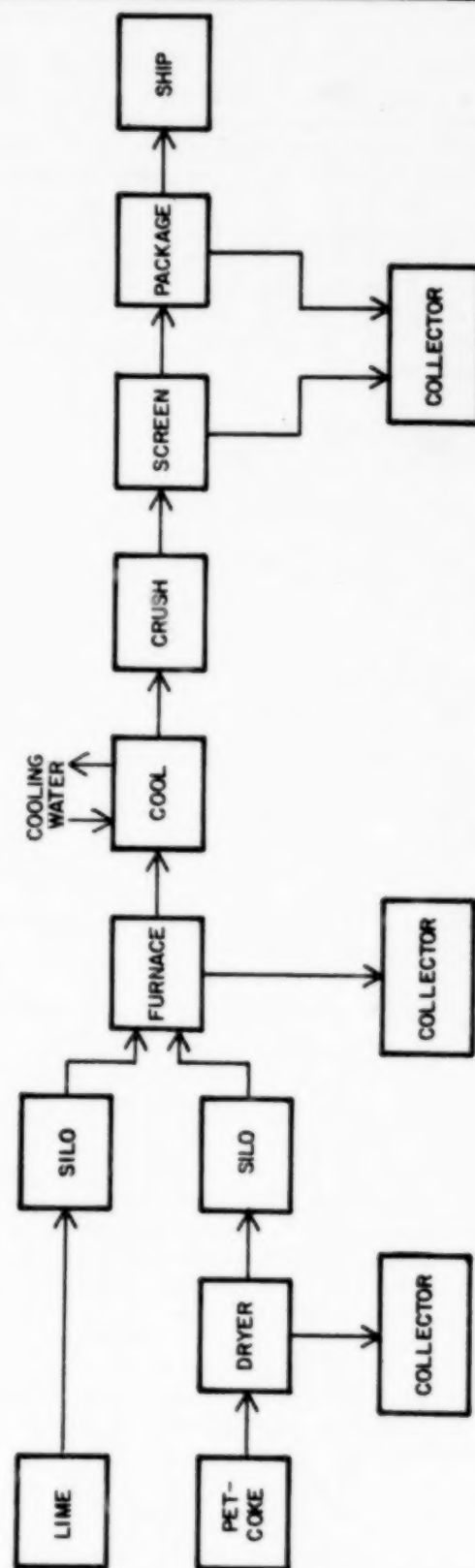


FIGURE 33  
CALCIUM CARBIDE PROCESS FLOW DIAGRAM AT PLANT 190

#### Waste Product

kg/kg of Product (lb/ton)  
Average Range

1. Fine Petroleum Coke	50 (100)	30-70 (30-140)
2. Stack Dust	85 (170)	70-115 (140-230)
3. Packing Dust	10 (20)	6-11 (12-22)
4. Cooling Tower Blowdown Solids and Cooling Water Treatment Chemicals		0.5-1 (1-2)

The first waste is collected by bag filters and recycled. Waste products 2 and 3 are now being exhausted to the air but will be collected and recycled by bag filters similar to those now collecting the coke fines. The fourth waste is currently untreated.

Figure 34 shows, schematically, the source and disposition of the water uses at this plant. Table 3 lists the effluent waste data supplied by plant 190 and verification measurements. (These data are the same as presented to the Corps of Engineers in plant 190's permit application, except for pH and flow, which were obtained during a plant visit).

Considerable amounts of chlorides and sulfates are discharged intermittently due to cooling tower blowdowns and use of water treatment chemicals.

Plant 190's policy is to recover and recycle all possible airborne dusts by dry collection techniques. This approach eliminates all process water wastes. The cooling tower blowdown and incoming water treatment regenerants are the only water effluents. There is no process waste water effluent in this exemplary plant.

#### Calcium Chloride

Calcium chloride is produced by extraction from natural brines. Some material is also recovered as a by-product of soda ash manufacture by the Solvay process. The latter will be discussed in the soda ash section.

In the manufacture of calcium chloride from brines, the salts are solution mined and the resulting brines are first partly evaporated to remove sodium chloride by precipitation. The brine is further purified by addition of other materials to remove sodium, potassium and magnesium salts by precipitation and further evaporation. It is then evaporated to dryness to recover calcium chloride which is packaged and sold. Figure 35 shows the detailed separation procedure used at plant 185. Bromides and iodides are first separated from the brines before sodium chloride recovery is performed. There is a large degree of brine

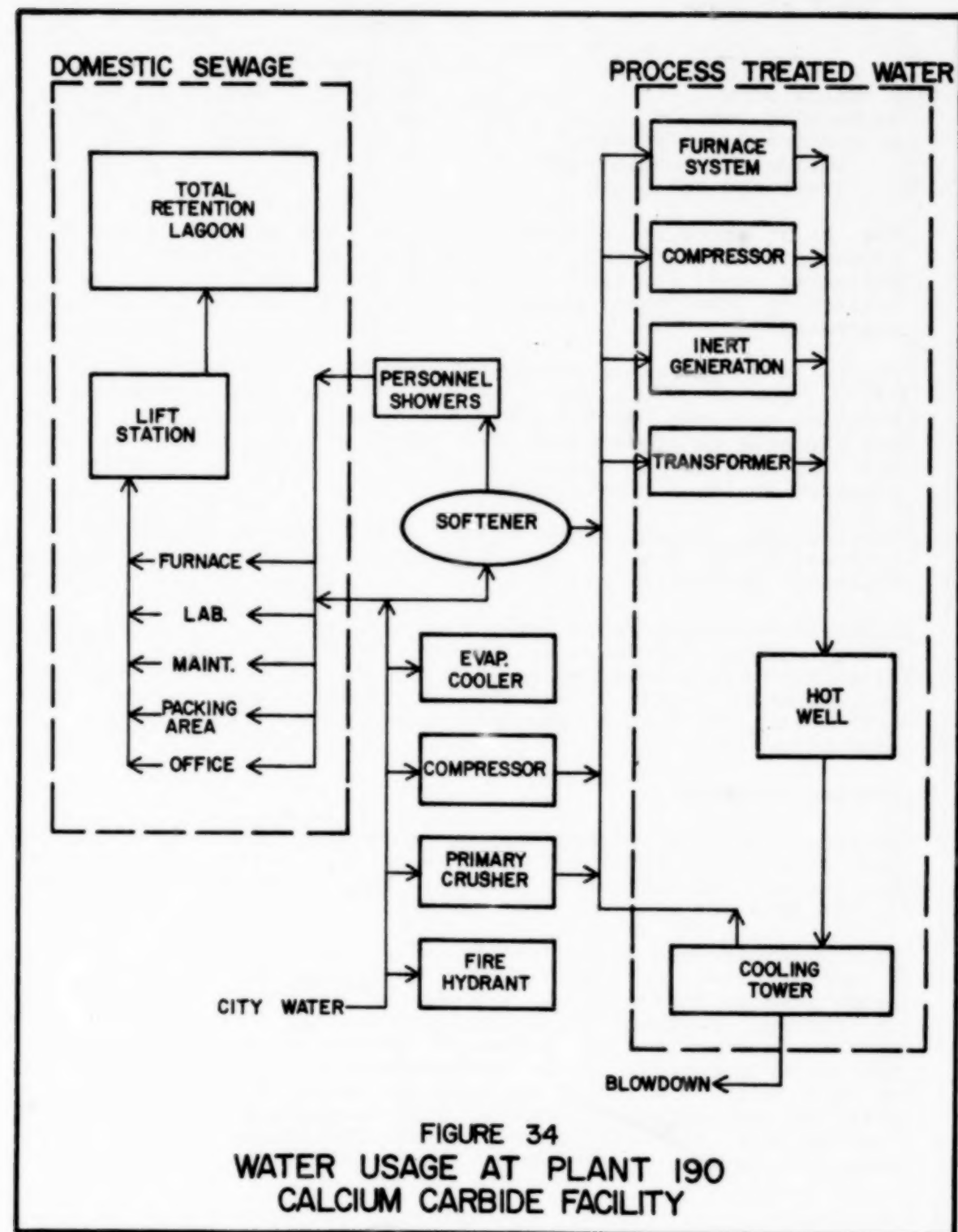


TABLE 3. Plant Effluent from CaC<sub>2</sub> Manufacture  
(All units ppm unless specified)

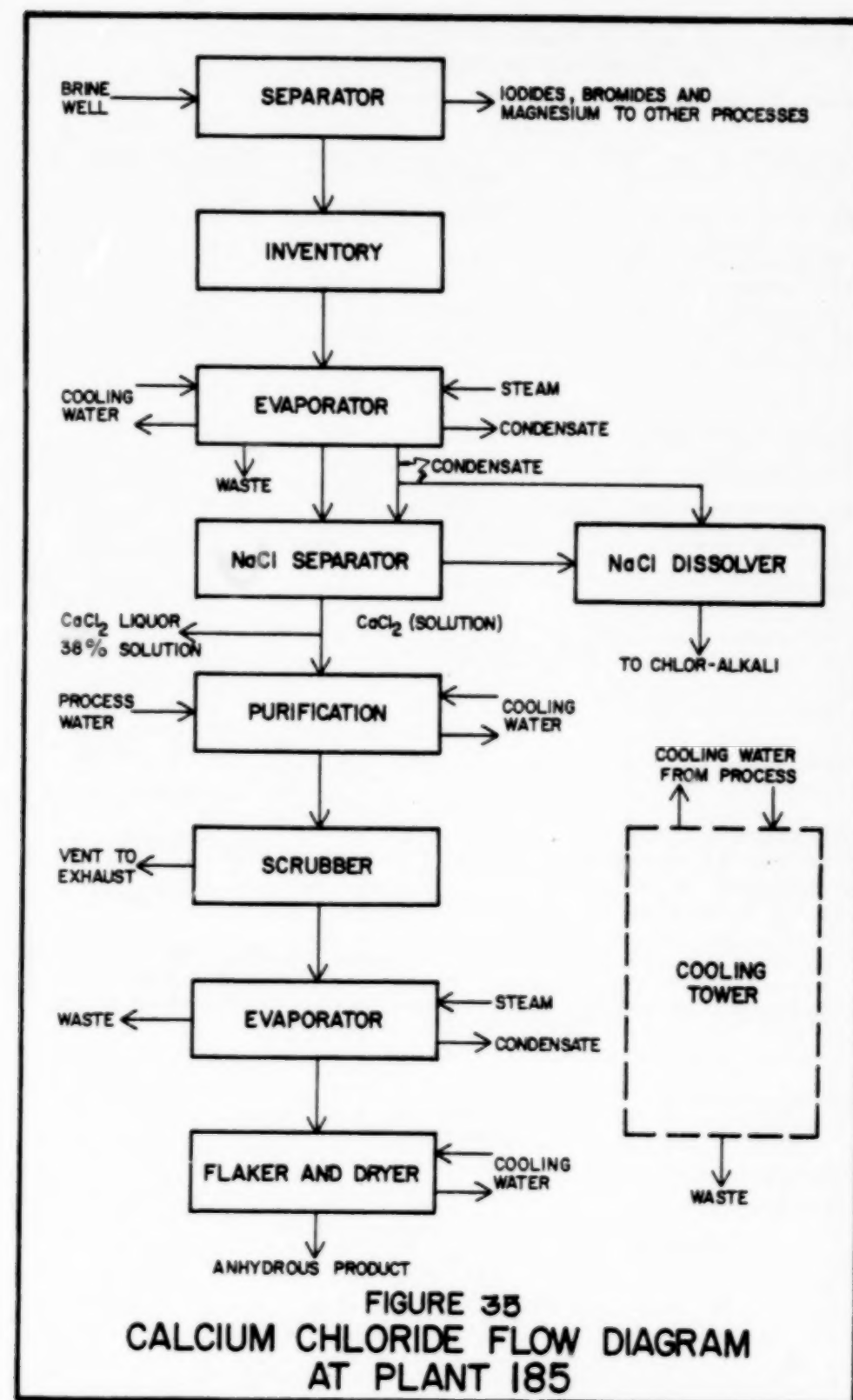
Parameter	Intake Water		Cooling Tower Water	
	Plant Data	Verifcn.	Plant Data	Verifcn.
Total suspended solids	3.5	0	48	0
Flow (cu m/day)	152	(a,b)	13	(a,b)
Total dissolved solids	238	(a)	1930	(a)
Conductivity (as NaCl)	(c)	95-100	(c)	810
BOD	80	(a)	308	(a)
COD	15	25	170	75
pH	7.6	7.5	7.6	8.0
Alkalinity (as CaCO <sub>3</sub> )	99	90	68	165
Nitrate (as N)	0.45	0.27	12	9.8
Zinc	0.01	(a)	2.8	(a)
Phosphorus Total (phosphate)	0.27	0.32	0.55	1.30
Color (APHA Units)	N11	10	675	20
Aluminum	0.15	(a)	0.17	(a)
Turbidity (FTU)	0	5	18	10
Fluoride	0.45	(a)	0.95	(a)
Total hardness (as CaCO <sub>3</sub> )	140	136	404	750
Calcium hardness (as CaCO <sub>3</sub> )	(c)	118	(c)	675
Sulfate	55	51.5	290	690
Chloride	46	36	198	95
Iron	0.03	0.08	-	0.019
Chlorine (as Cl <sub>2</sub> )	(c)	0	(c)	0.1

(a) Not measured

(b) Flow varied frequently, depending on response of level-monitoring valve

(c) Not in furnished data.

Note: Above data are not from split samples, but represent data furnished for Corps of Engineer permit application approximately two years prior to the verification measurements.



recycling to remove most sodium chloride values. The composition of the brine is:

CaCl <sub>2</sub>	19.3 percent
MgCl <sub>2</sub>	3.1 percent
NaCl	4.9 percent
KCl	1.4 percent
Bromides	0.25 percent
Other minerals	0.5 percent
Water	70.6 percent

The raw wastes expected from calcium chloride manufacture at plant 185 arise from blowdowns as well as from the several partial evaporation steps used. Most of the wastes are weak brine solutions:

Waste Products	Process Source	Avg. kg/kg of Product (lb/ton)
NH <sub>3</sub>	Evaporators	0.55 (1.1)
CaCl <sub>2</sub>	Evaporators	29 (58)
NaCl	Evaporators	0.5 (1.0)
CaCl <sub>2</sub>	Packaging	0.7 (1.4)
*NaCl & KCl	Brine Separation	45.5 (91)
*NaCl	Secondary Brine Separation	110 (220)

\*Recycled or used elsewhere.

At plant 185, the waste brine streams are passed through an activated sludge treatment to remove organics and are then passed to a settling basin to remove suspended matter, adjusted to neutral pH, fed into a second pond to further settle suspended matter, and finally discharged. Future plans at plant 185 call for changes in the evaporators to reduce calcium chloride discharges and eliminate ammonia from the discharges. More recycling of spent brines is also planned. Table 4 gives a detailed breakdown of current water usage at plant 185.

Table 4A lists the river intake and effluent compositions at plant 185. The effluent consists mostly of weak brine solutions (neutral pH).

#### Calcium Oxide and Calcium Hydroxide

Calcium oxide is manufactured by thermal decomposition of limestone in a kiln. The limestone is first crushed, then added to the kiln, wherein it is calcined to effect decomposition. The product is then removed from the kilns, marketed as is, or slaked by reaction with water to produce calcium hydroxide. A process flowchart is given in Figure 36 descriptive of the general process at plant 007.



TABLE 4. Plant 185 Water Flows

## A. Inputs

Type	cu m/day (MGD)	liters/kg (gal/ton)
River (+ 44%)	31,100 (8.208)	62,700 (15,000)
Lake	545 (0.144)	1,100 (263)

## B. Water Usage

Type	cu m/day (MGD)	liters/kg (gal/ton)	% Recycled
Cooling	58,500 (15.5)	118,000 (28,300)	46
Process	164,000 (43.2)	330 (79)	0
Washdown	2,180 (0.576)	4,390 (1,052)	0
Washout	680 (0.180)	1,370 (329)	10

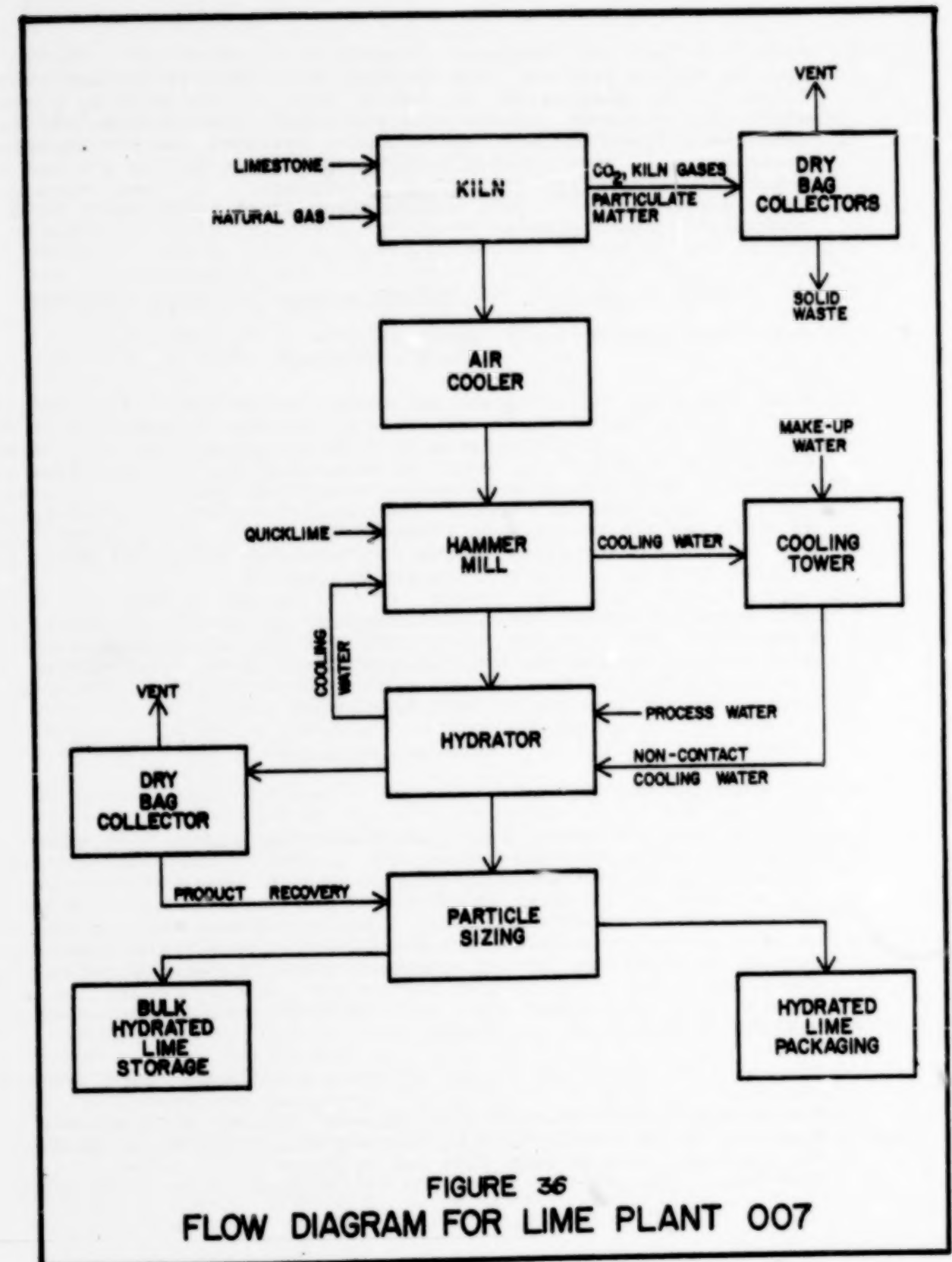
TABLE 4A Composition of Intake and Effluent Stream of Plant 185

Parameter*	Intake		Effluent Stream No. 1	
	Plant Data	Verification Measurement	Plant Data	Verification Measurement
Flow, cu m/day (MGD)	31,600 (8.35)	**	31,600 (8.35)	**
Total Suspended Solids	42	8	-	29
Total Dissolved Solids	353	293	2,693	309
BOD	3	-	1.1	-
COD	-	-	-	-
pH	8.3	8.3	6.7-8.0	9.1
Turbidity (FTU)	5.3	0	18.2	25
Color (ALPH Units)	20	70	60	80
Conductivity (NaCl)	476	520	5,390	340
Hardness (Ca)	200	179	700	169
Sulfate	110	36	312	36
Nitrate	0.2	0.29	0.2	20
Ammonia	0.1	0.60	2.0	8.8
Organic Nitrogen	0.2	-	2.7	-
Iron	0.4	0.30	1.0	0.09
Copper	-	-	-	-
Chromate	0.1	-	0.1	-
Manganese	0.05	-	0.1	-
Zinc	0.1	-	0.85	-
Total Alkalinity (CaCO <sub>3</sub> )	160	170	67	235

\* mg/l unless otherwise specified

\*\*measurement not possible due to physical constraints of location

Note: Above data not split samples; plant data furnished separately, prior to sampling for verification.

FIGURE 36  
FLOW DIAGRAM FOR LIME PLANT 007

The raw wastes produced from calcium oxide manufacture are shown below. The quantities of waste are not affected by process startup or shutdown. These consist of fine dusts collected from the plant gas effluent by scrubbing systems. At the exemplary facility, this dust removal is achieved by use of bag filters and other dry particulate collection equipment. No wet scrubbing techniques are employed. Wet scrubbing of these dusts is used commonly at other plants.

<u>Waste Product</u>	<u>Process Source</u>	<u>kg/kkg of Product (lb/ton)</u>
Dry Particulate Matter	Kiln gases (Dry collector)	67 (133)

Exemplary plant water usage is described below. All cooling water is recycled and all product water is consumed in the manufacture of calcium hydroxide. Due to the use of dry waste collection techniques, there is no waterborne effluent from the facility. This plant achieves ninety-five percent or better solids collection at the kiln collector. Municipal water intake to the plant amounts to 638 l/kkg (153 gal/ton) of product plus the amount evaporated in the cooling tower. This water is not further treated in the plant prior to use.

This water represents the process water, which is used in the hydrator. The cooling water flow for the bearings on the tube mill and pistons on the hydrator pump amounts to 1000 l/kkg of product (240 gal/ton). It is completely recycled with makeup water added to compensate for evaporation.

Chlorine and Sodium or Potassium Hydroxide

#### a) Mercury cell process

Caustic and chlorine are produced from sodium chloride or potassium chloride raw materials in the mercury cell process, depending on whether caustic soda or caustic potash is to be produced. The raw material is dissolved and purified by addition of barium carbonate, soda ash, and lime to remove magnesium and calcium salts and sulfates prior to electrolysis. The insolubles formed on addition of the treatment chemicals are filtered from the brine. The brine is then fed to the mercury cell, wherein chlorine is liberated at one electrode and a sodium-mercury amalgam is formed at the other.

The chlorine formed is cooled, dried in a sulfuric acid stream, purified to remove chlorinated organics, compressed and sold. The mercury-sodium amalgam also formed during electrolysis is sent to a "denuder" where it is treated with water to decompose the amalgam. Sodium hydroxide and hydrogen are formed in the reaction. The mercury liberated is returned to the electrolysis

cells. The hydrogen is cooled, scrubbed to remove traces of mercury, compressed and sold.

The sodium hydroxide formed at the denuders is filtered, concentrated, and sold. Brines emerging from the electrolysis cells are concentrated and recycled.

Two exemplary facilities, plants 130 and 144, and one qualified exemplary facility, plant 098, have been selected and studied in detail. Plant 130 produces potassium hydroxide and plants 144 and 098 produce sodium hydroxide. Plant 098 is considered as an exemplary plant with the qualification that it is located outside of the United States. It is included because its mercury recovery system is of special note. The process flow diagram for plant 130 is shown in Figure 37.

Raw waste loads for this process are presented in Table 5, which gives overall figures based on twenty-one facilities, plus partial data as furnished from plants 098 and 130. The chief raw wastes include purification muds ( $\text{CaCO}_3$ ,  $\text{Mg(OH)}_2$  and  $\text{BaSO}_4$ ) from brine purification, some spent brine materials from caustic recovery, and condensates from chlorine and hydrogen compressions. The sulfuric acid used to dry the chlorine is not a waste in plant 130 as it is recovered for sale.

In the caustic potash plant, plant 130, the brine muds and potassium chloride make up the bulk of the primary waste. A small amount of copper sulfate catalyst is also wasted. This catalyst is used in treatment of waste chlorine. Specifically, the chlorine is reacted with excess sodium hydroxide in the presence of copper sulfate to produce sodium chloride, water and oxygen. The sodium chloride so produced is sent to the waste treatment facilities.

At plant 144, the wastes emerging from chlor-alkali manufacture are sent to a series of two settling ponds, with the exception of those from the cell building, which are sent to a mercury treatment unit first. The wastes from chlorine drying, brine preparation, salt saturation and caustic loading are sent directly to the two settling ponds described above, where suspended solids are removed and the pH adjusted prior to discharge. Two emergency ponds are in parallel with these two ponds and wastes can be diverted to them for special treatment if needed.

Mercury-containing wastes from the cell building are first treated prior to being sent to the central waste treatment system. The effectiveness of treatment based on six months of data (129 days of measurements) is, in summary:

	<u>Mercury Concentration to Secondary Treatment (mg/l)</u>	<u>Mercury Concentration after Treatment (mg/l)</u>	<u>Average Removal Efficiency (percent)</u>
Average	44.3	0.43	99.0
Maximum values	1920.0	15.0	-
Minimum values	0.48	0.01	-

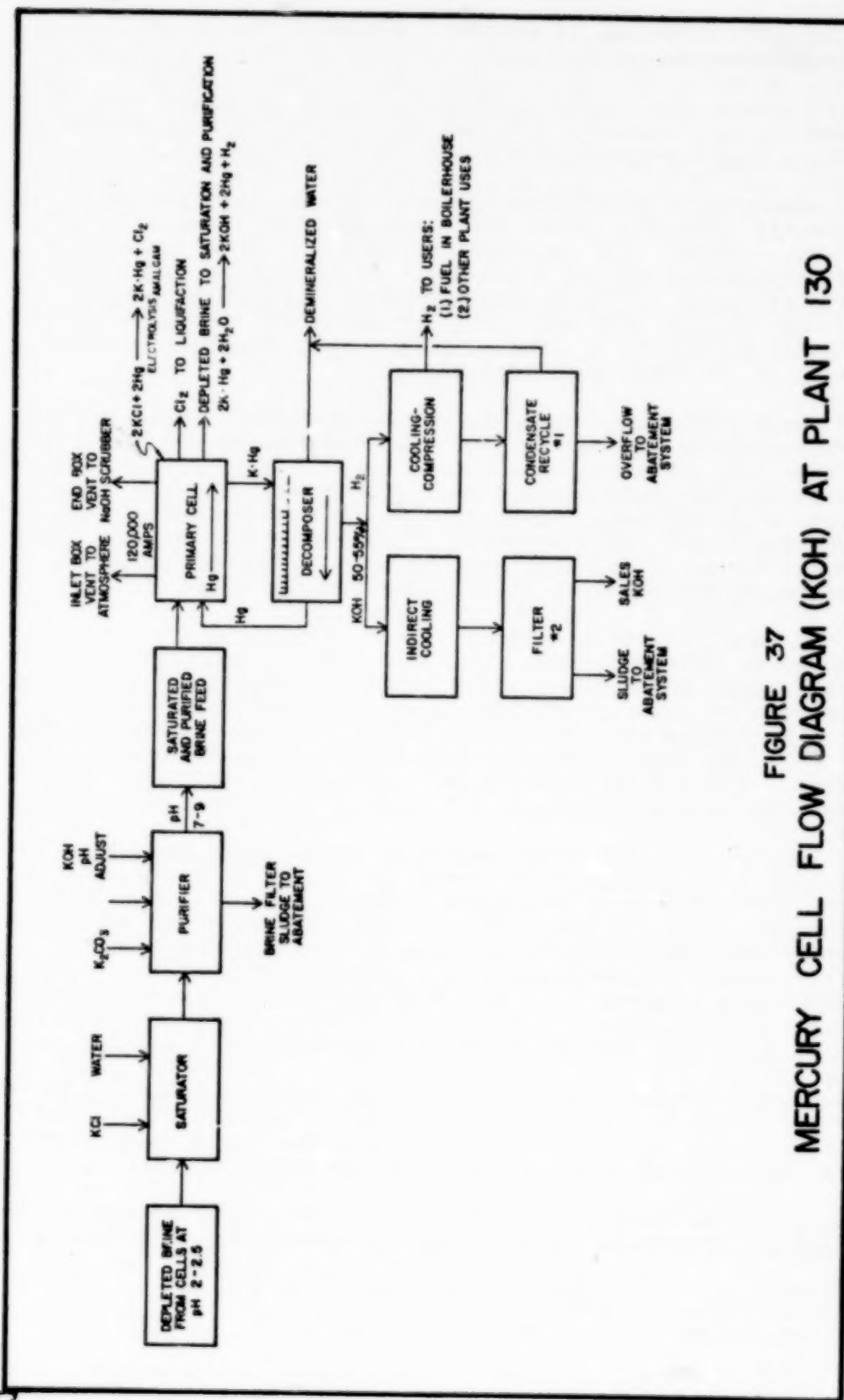


FIGURE 37  
MERCURY CELL FLOW DIAGRAM (KOH) AT PLANT 130

TABLE 5. Raw Waste Loads from Mercury Cell Process  
(All Amounts in kg/kg of Chlorine)\*

	Based on 21 Facilities		Plant 098	Plant 130	
	Mean	Range		Mean	Range
Purification muds, CaCO <sub>3</sub> & Mg(OH) <sub>2</sub>	16.5	0.5-35	7.25	7.5	6.8-7.9
NaOH	13.5	0.5-32	-	-	-
NaCl	211	15-500	-	40	35-45
KCl	0	-	0	50	45-54
H <sub>2</sub> SO <sub>4</sub>	16	0-50	11.3	0	-
Chlorinated Hydro-carbons**	0.7	0-1.5	-	-	-
Na <sub>2</sub> SO <sub>4</sub>	15.5	0-63	-	-	-
Cl <sub>2</sub> (as CaOCl <sub>2</sub> )	11	0-75	-	-	-
Filter aids	0.85	0-5	1.83	-	-
Mercury	0.15	0.02-0.28	0.0018	-	-
Carbon, graphite	20.3	0.35-340	-	-	-
CuSO <sub>4</sub>	0	-	0	0.004	-

\*can be converted to lb/ton of product by multiplication by 2.0.

\*\*depends markedly on grade of chlorine produced.



Approximately 99 percent removal of mercury is achieved with the mercury losses from the facility being kept to about 0.0045-0.0237 kg/day (0.01-0.05 lb/day) for the most part. Figure 38 gives a histogram of the mercury discharges on a daily total quantity basis. The mean value of this discharge parameter is 0.0178 kg/day (0.03882 lb/day) or 0.000070 kg/kg of chlorine (0.000140 lb/ton of chlorine). Ninety-one percent of the measurements fell below 0.00014 kg/kg.

At plant 098, several of the streams are completely recycled to minimize brine wastes. Treatment of mercury-containing streams makes use of sodium sulfide to precipitate mercury and mercury sulfides. These materials are filtered from the streams, recovered as solids and treated with sodium hypochlorite to recover mercury (as chloride). The leached solids can then be safely discarded and the mercury chloride-containing solutions can be used for brine makeup and returned to the cells where the mercury chloride is decomposed to elemental mercury for reuse.

The mercury effluent and chlorine treatment effectiveness at plant 098 are as follows:

Method	Qualitative Rating*	Waste Reduction Accomplished
Mercury Recovery Unit	Excellent	97 percent recovery of mercury
Chlorine Neutralization System	Excellent	100 percent removal of chlorine from waste gas stream
Hydrogen Peroxide Treatment of liquid effluent	Good	100 percent removal of available chlorine

\*As rated by plant personnel.

The mercury discharged and recovered from the sulfide treatment system over a two month period in 1972 from this plant averaged 0.0108 kg/day (0.0237 lb/day) or 0.000069 kg/kg (0.000138 lb/ton) of chlorine. Analysis of the data for the two month period showed that the average mercury recovery was 258 kg/day (568 lb/day) or 7.5 kg/kg (15.0 lb/ton) of chlorine. At the plant 130 mercury cell facility, brine filter sludges, potassium hydroxide recovery wastes and other waste streams are fed into a common treatment system, wherein the wastes are treated with sodium hydrosulfide and flocculants. The insoluble mercury products from treatment are removed by settling and filtration and the wastes are then discharged. The mercury content of the

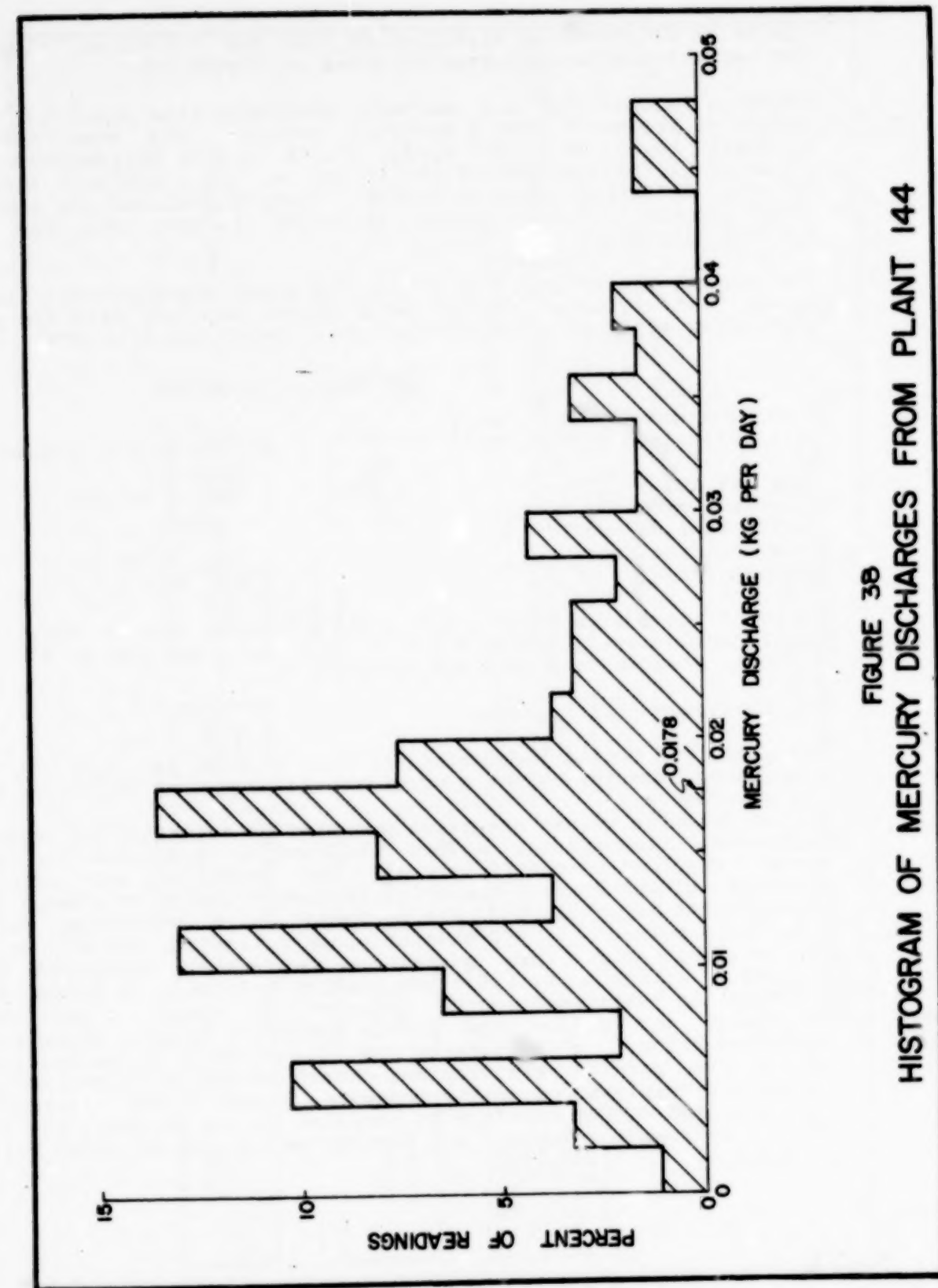


FIGURE 38  
HISTOGRAM OF MERCURY DISCHARGES FROM PLANT 144

Table 6 summarizes the mercury effluents from plant 130 as a result of treatment over a one-year period. The mean mercury effluent level of 0.0073 kg/day (0.016 lb/day) corresponds to a value of 0.000057 kg/kg (0.000114 lb/ton) of chlorine, similar to the 0.000069 kg/kg (0.000138 lb/ton) calculated for the 098 plant and the 0.000070 kg/kg (0.000140 lb/ton) for the 144 mercury cell plant.

The general characteristics of the 098 plant discharge are listed below. The seawater cooling water stream is mixed with the process water effluent prior to discharge, hence the high TDS:

	<u>Average</u>	<u>Range</u>
Total Suspended Solids, mg/l	5	5-10
Total Dissolved Solids, mg/l	-	20,000-25,000 (seawater)
pH	7.1	6.7-8.5
Temperature, °C (°F)	12 (54)	10-19 (50-66)
Hydrogen Peroxide, mg/l	0	0-1.0
Sodium Sulfide, mg/l	0	0-0.5
Free Chlorine, mg/l		Max. 0.08
Mercury, mmq/l		Max. 8.0

Tables 7 and 8 give the plant 130 effluent stream data and verification data. Tables 9 and 10 give the plant 144 intake and effluent streams data with verification data.

## b) Diaphragm cell process

The plant 057 facility described in this section is part of an integrated complex using a considerable amount of recycling and reuse technology.

Sodium chloride brines are first purified by addition of sodium carbonate, flocculating agents and sodium hydroxide in the amounts required to precipitate all the magnesium and calcium contents of the brine. The brine is then filtered to remove the precipitated materials and electrolyzed in a diaphragm cell. Chlorine, formed at one electrode, is collected, cooled, dried with sulfuric acid, then purified, compressed, liquified and shipped. At the other electrode, sodium hydroxide is formed and hydrogen is liberated. The hydrogen is cooled, purified, compressed and sold. The sodium hydroxide formed, along with unreacted brine, is evaporated to 50 percent concentration. During the partial evaporation, most of the unreacted sodium chloride precipitates from the solution, which is then filtered. The collected sodium chloride is recycled to the process, and the sodium hydroxide solutions are further evaporated to yield solid products.

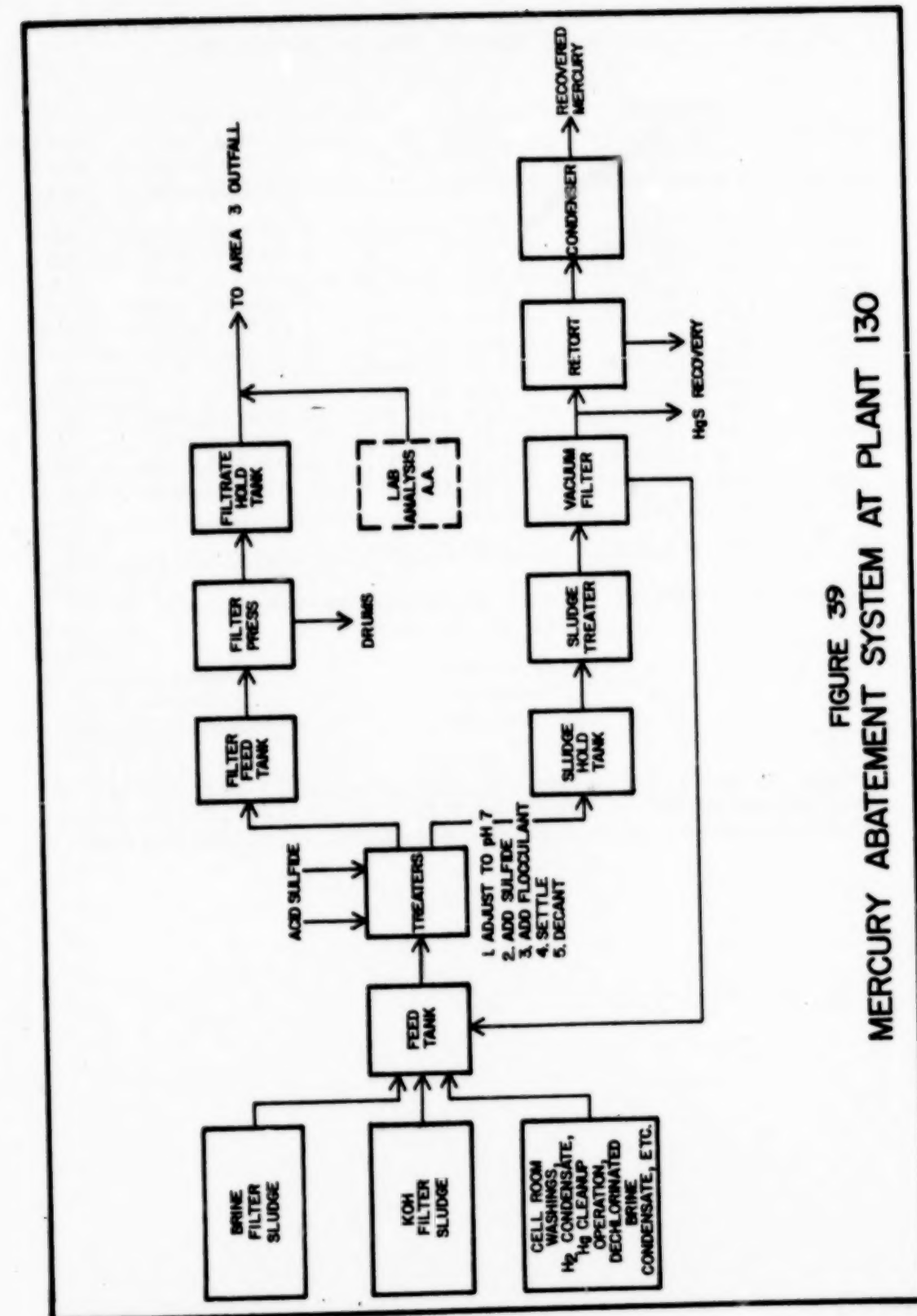


FIGURE 39  
MERCURY ABATEMENT SYSTEM AT PLANT 130

TABLE 6. Monthly Mercury Abatement System Discharge  
During 1972 at Plant 130

Month	Average Volume Discharge cu m (gal)/day	Total Hg Discharge kg (lb)	Average Daily Hg Discharge kg (lb)/day	Average mcg/l Hg
Jan	144 (37,916)	0.369 (0.813)	0.012 (0.026)	82
Feb	118 (31,030)	0.327 (0.719)	0.011 (0.024)	92
Mar	92 (24,195)	0.198 (0.435)	0.0064 (0.014)	69
Apr	112 (29,616)	0.184 (0.404)	0.0059 (0.013)	53
May	115 (30,339)	0.318 (0.700)	0.010 (0.023)	91
Jun	134 (35,277)	0.214 (0.471)	0.0068 (0.015)	51
Jul	124 (32,709)	0.225 (0.494)	0.0073 (0.016)	59
Aug	137 (36,169)	0.302 (0.665)	0.0096 (0.021)	72
Sep	131 (34,435)	0.127 (0.280)	0.0041 (0.009)	31
Oct	129 (34,024)	0.133 (0.293)	0.0041 (0.009)	33
Nov	126 (33,339)	0.176 (0.377)	0.0055 (0.012)	43
Dec	118 (31,135)	0.144 (0.251)	0.0036 (0.008)	31
Av.	123 (32,516)	0.224 (0.492)	0.0073 (0.016)	59

Statistical Summary: Mercury Abatement System Jan-Aug 1972 -  
Total of 244 Days

	Daily Mercury Discharge, kg (lb)/day	Daily Volume Discharge, cu m (gal)/day
Mean	0.0086 (0.019)	122 (32,164)
Range, Max.	0.0545 (0.120)	292 (63,945)
Standard Deviation	0.0077 (0.017)	40 (10,492)
90% of Values	0.0182 (0.040)	173 (45,594)

TABLE 7. Plant 130 Effluent Data\*

	Outfall #1	Outfall #2	Outfall #3**	Intake
Flow, cu m/day (MGD)	9,460 (2.5)	13,300 (3.5)	42,400 (11.2)	-
Total Suspended Solids	5	-	-	-
pH	8-11	8-9	8-9	-
Color (APHA Units)	-	-	-	5
Conductivity, umhos	-	-	-	287
Hardness, (Total) (CaCO <sub>3</sub> )	-	-	400	134
Chloride	-	-	1252	22
Free Chlorine	-	-	0	0
Fluoride	-	-	1	1
Phosphates (as P)	-	-	-	0.1
Nitrate (as N)	-	-	1.92	1.92
Iron	-	-	1.2	1.0
Copper	-	-	-	0.01
Chromium	-	-	0.01	0.01
Manganese	-	-	-	-
Vanadium	-	-	-	-
Arsenic	-	-	-	0.28
Mercury, mcg/l	-	-	1.2	1
Lead	-	-	0.1	0.1
Sulfate	-	-	39	18
Turbidity	-	-	-	16

\*Data supplied by Plant 130, mg/l unless otherwise specified.  
\*\*Main outfall, outfalls 1 & 2 feed into 3. This waste stream  
contains potassium carbonate manufacturing effluent also.



TABLE 8. Measurements of the Effluents  
From Plant 130

Parameter*	River (Intake)	Hg Cell Chlorine Liquefaction**	Abatement**	Major Outfall**
Flow, cu m/day (MGD)	Not Measured	8,540 (2.25)	16,700 (4.28)	42,000 (11.1)
Temp., °C	2.0	11.95	10.1	8.5
Color, Apparent, APHA Units	60	60	180	150
Turbidity, FTU	23	19	55	50
Conductivity, mhos/cm	230	240	320	370
Suspended Solids,	70	210	75	210
pH	7.8	11.9	9.4	10.5
Alkalinity (Total)				
P (CaCO <sub>3</sub> )	0	40	30	25
T (CaCO <sub>3</sub> )	97	180	135	200
Hardness, (Total)				
(CaCO <sub>3</sub> ) mg/l	145	60	140	65
Calcium (CaCO <sub>3</sub> )	115	25	110	35
Chlorine	0	0.2	0.3	0
Chloride	35	47.5	60	48.5
Fluoride	0	0	0	0
Sulfate	45	44	41	40
Phosphates (Total)	0.38	0.4	0.42	0.37
Nitrogen (Total)	1.55	0.45	0.13	0.38
Iron	0.19	0.5	0.7	0.4
Dissolved oxygen	***	8.3	7.6	8.5
Mercury, mcg/l	5	5	5	5

\*mg/l unless otherwise specified.

\*\*Corresponds to outfalls #1, 2 and 3 respectively on Table 21.

\*\*\*Unable to determine at temperature below 5°C.

TABLE 9. Plant 144 Intake Water

Parameter*	Plant Data**	GTC Measurement
Temperature, °C	8-24	19
Color, Apparent, APHA Units	-	175
Turbidity, FTU	-	50
Conductivity, mhos/cm	75	55
Suspended Solids	10	10
Dissolved Solids	65	-
pH	6.6	6.7
Acidity: Total	-	0 CaCO <sub>3</sub>
Free	-	0 "
Alkalinity (Total) P	-	0 "
T	18	16 "
Hardness: Total	-	15 "
Calcium	-	5 "
Halogens: Chlorine	-	0.18
Chloride	-	15
Fluoride	-	0.1
Sulfate	-	8
Phosphates (Total)	-	0.34
Heavy Metals: Iron	-	0.48
Chromate (Cr+6)	-	0.02
Oxygen (Dissolved)	-	12
COD	15	10

\*mg/l unless otherwise specified.

\*\*Data from Corps of Engineers permit application, approximately two years prior to verification sampling.

TABLE 10. Plant 144 Effluent Data

Parameter*	Plant Data**	Verification Measurement
Flow, cu m/day (MGD)	5,300 (1.9)	8,360 (3.0)
Temperature, °C	32-38	33
Color, Apparent, APHA Units	-	30
Turbidity, FTU	-	10
Conductivity, mhos/cm	1,525	2,000
Suspended Solids	0	0
Dissolved Solids	1,455	1,777
pH	7.0	7.5
Acidity: Total	-	0 CaCO <sub>3</sub>
Free	-	0 "
Alkalinity (Total) P	-	0 "
T	60	14 "
Hardness: Total	-	20 "
Calcium	-	10 "
Halogens: Chlorine	-	0
Chloride	-	1020
Fluoride	-	0.5
Sulfate	-	107
Phosphates (Total)	-	0.18
Heavy Metals: Iron	-	0.42
Chromate (Cr+6)	-	0.02
Oxygen (Dissolved)	-	10
COD	8	5
Mercury, mcg/l	3	5

\*mg/l unless otherwise specified.

\*\*Data from Corps of Engineers permit application, approximately two years prior to verification sampling.

Figure 40 shows the flow diagram of a 1810 kkg/day (2000 ton/day) chlorine-caustic soda plant. A new 2080 kkg/day (2300 ton/day) chlorine-caustic soda plant also exists in this facility. The sodium hydroxide product from these two plants is concentrated in another portion of plant 057. This function is illustrated in Figure 41. All three of these facilities (all parts of plant 057) will be discussed below.

There are no brine wastes from plant 057 and several of the other waste streams are diverted for other uses in the complex. This stream diversion and maximal raw material utilization has served to minimize the wastes to be treated. The raw wastes from the newer plant are:

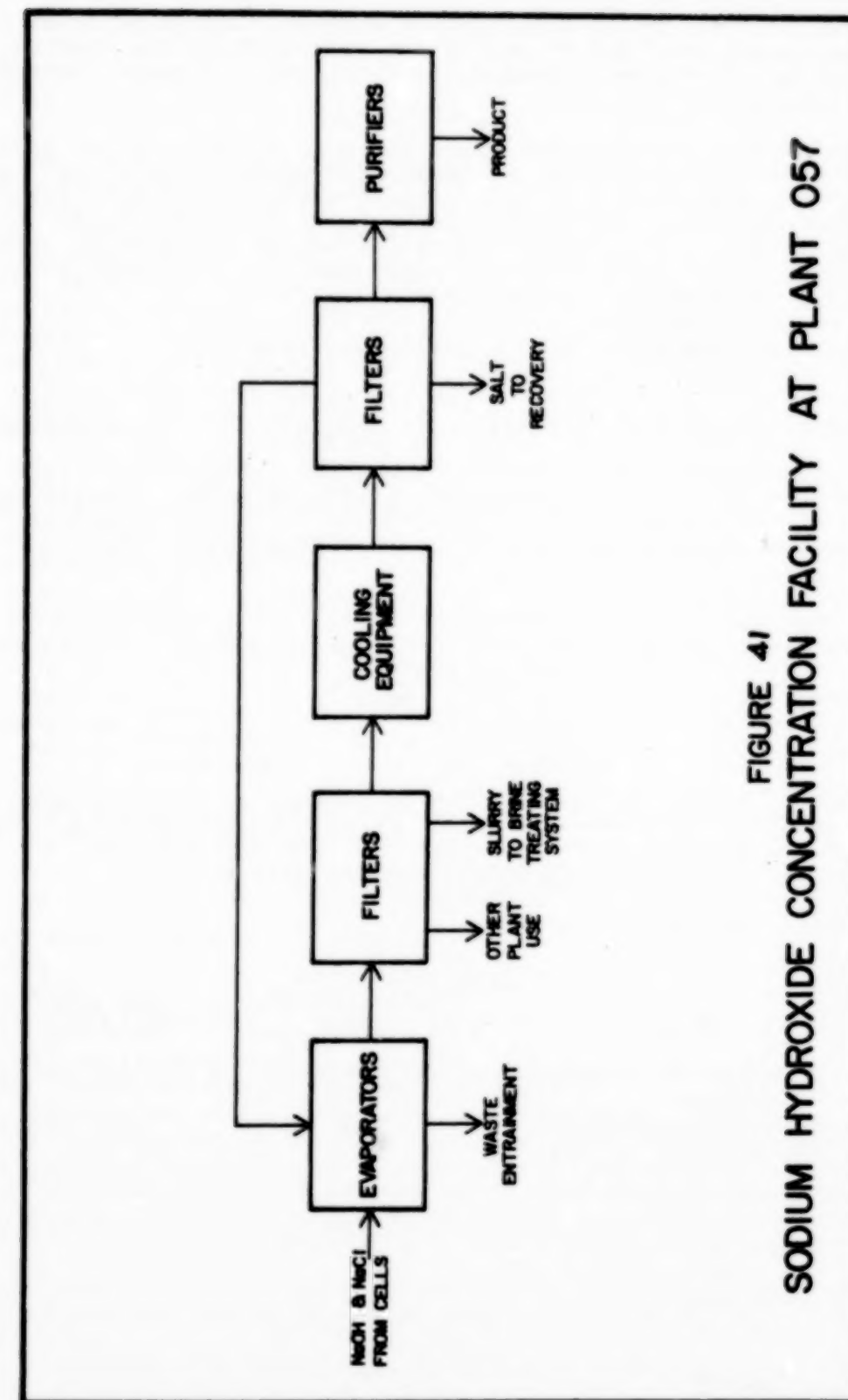
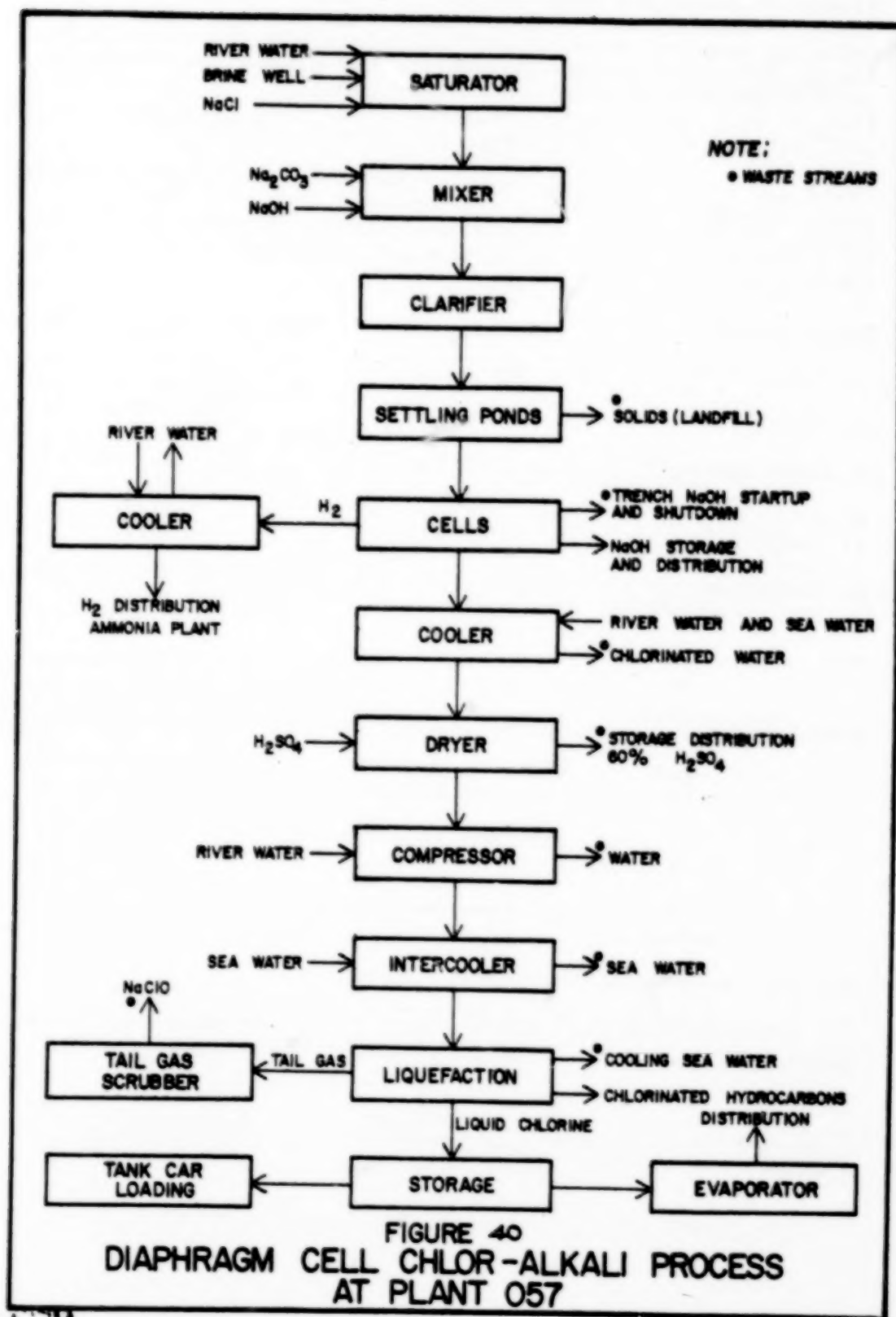
Waste Product	Process Source	Ave. kg/kkg (lb/ton) of Cl <sub>2</sub>
1. NaOCl	Gas Scrubber	1.13 (2.26)
		(Startup and shutdown)
2. NaHCO <sub>3</sub>	Gas Scrubber	2.49 (4.58)
		(Wastes are ponded for recycle)
3. Chlorinated Organics	Liquefaction	0.35 (0.70)
4. Brine Sludge	Brine Treatment	10.5 (21)
5. Spent Sulfuric Acid	Chlorine Drying	1.0 (2.0)
6. Chromates	Cooling Tower	0.000363 (0.000726)
7. Suspended Solids	Cooling Tower	0.0333 (0.0666)

The raw wastes from the old plant are:

Waste Product	Process Source	Average kg/kkg of Chlorine (lb/ton)
1. Weak Caustic	Cells	66.25 (12.5)
2. Spent Sulfuric Acid	Chlorine Drying	4.05 (8.1)
3. NaOCl	Tail Gas Scrubber	7.50 (15.0)
4. Carbonate Sludge (CaCO <sub>3</sub> )	Brine Treating	12.25 (24.5)
5. Chlorinated Hydrocarbons	Chlorine Purification	0.70 (1.4)

The raw wastes from the caustic plant are:

Waste Products	Process Source	Average kg/kkg of Product (lb/ton)
1. NaOH	Entrainment	4.4 (8.8)
2. NaCl	Entrainment	5.1 (10.2)
3. NaOH	Filter Wash	17.6 (35.2)
4. NaCl	Filter Wash	20.3 (40.6)





Many of the chlor-alkali waste streams, including brine wastes, are either recycled or put to use elsewhere in the complex. This section discusses treatment of those streams which are discharged.

The newer chlor-alkali plant takes in 2,720 cu m/day (0.72 mgd) of river water for cooling makeup and process water, as well as 54 cu m/day (0.0144 mgd) of well water for potable use. About 98.5 percent of the total cooling water flow of 109,000 cu m/day (28.8 mgd) is recycled, and 90 percent of the process water flow of 6040 cu m/day (1.6 mgd) is recycled. Of the potable water intake, 10 percent is recycled.

The waste treatment within this newer plant is:

<u>Stream No./Source</u>	<u>Flow, l/day (gpd)</u>	<u>Treatment Method</u>	<u>Final Disposal</u>
1/Gas Scrubber	409,000 (108,000)	Sunlight decomposition of NaOCl	To plant waste water system
2/Spent Sulfuric Acid	2,890 (765)	Other plant use	Used
3/Chlorine liquefaction	492 (130)	Incineration	---
4/Brine Treating	327,000 (86,400)	Solids to landfill	Brine recycled
5/Cooling Tower Blowdown	75,700 (20,000)	None	To plant waste water system

Waste chlorine in the tail gas is reduced by 80 percent in an absorption process, and the remaining chlorine is removed by scrubbing. These two processes are used in series to attain complete removal of chlorine from the tail gas.

Future treatment plans are:

<u>Method</u>	<u>Estimated Installation Time</u>	<u>Estimated Performance</u>
1. Chlorinated hydrocarbon waste burner	2 years	100 percent
2. Catalytic conversion of scrubber effluent to remove sodium hypochlorite	1 year	100 percent
3. Neutralization of scrubber effluent to remove sodium carbonate	1 year	100 percent

At the older chlor-alkali facility in plant 057, river water intake is 10,450 cu m/day (2.76 mgd) and seawater intake is 57,200 cu m/day (15.14 mgd). The cooling water flow is 61,000 cu m/day (16.13 mgd), which is all non-contact except for the water chlorination step. Process water flow is 6,530 cu m/day (1.726 mgd), which is mainly as brine. Other process water uses are compression cooling, hydrogen cooling, chlorine cooling and absorption. There is less recycling of water here than in the newer plant. The effluent stream which is not recycled arises from the tail gas scrubber, which has a flow of 133,000 l/day (35,000 gal/day) or 141 l/kg (37.2 gal/ton) based on chlorine product. This is disposed of completely in the plant waste system. It contains sodium hypochlorite. The disposal of this material will be eliminated and the tail gas will be used to manufacture hydrochloric acid product, thus eliminating a waste stream. When this happens, the older process should be close to a nondischarge system.

The water intake to the caustic plant is:

	<u>cu m/day (mgd)</u>
river water	1,890 (0.50)
seawater	90,900 (24.0)
well water	57 (0.015)

The river water is treated; the well water is not. The in-plant water flows are:

	<u>cu m/day (mgd)</u>	<u>% Recycled</u>
Forced Draft Cooling	6,540 (1.73)	95
Process	1,300 (0.344)	0
Washdowns	265 (0.070)	0
Entrainment Seawater	90,900 (24.0)	0

The only effluent to be treated is 4.4 kg/kg (8.8 lb/ton) of sodium hydroxide and 5.1 kg/kg (10.2 lb/ton) of sodium chloride in a 90,900 cu m/day seawater waste stream (the entrained system). This system is presently discharged without treatment. Future plans call for it to be neutralized prior to discharge. Chloride values entrained in this stream are considered to be too low to be worthwhile for other plant usage. These three facilities are being improved to further reduce discharges.

The effluents from the newer chlor-alkali facility, the older facility and the sodium hydroxide plant are shown below.

Newer Plant:

Parameter	Average Concentration, mg/l				
	Stream No. 1	2	3	4	5
Total Dissolved Solids	18,330 (mostly chlorides)	-	-	1200	820
Total Suspended Solids	14	-	-	22,500	256
BOD	0	0	0	0	0
CCD	0	0	0	0	0
pH	7.8	1	-	11.0	7.0
Temperature, °C	38	Ambient	31	Ambient	32
Chromate	-	-	-	-	10

Older Plant:

Dissolved Solids 103,090 (chlorides, hypochlorites)

Alkali Plant:

NaOH 25  
NaCl 28.9 (added to seawater)

Hydrochloric Acid

Hydrochloric acid is manufactured principally by two processes: (1) As a by-product of organic chlorinations; and (2) By direct reaction of chlorine with hydrogen. Only production by direct reaction of chlorine is considered herein. In this process, hydrogen and chlorine are reacted in a vertical burner. The hydrogen chloride formed is condensed in an absorber from which it flows to a storage unit for collection and sale. The arrangement used at the exemplary facility (plant 121) is similar to the standard flow diagram shown in Section IV. The special waste treatment system used during startup of this facility startup is shown in Figure 42.

The raw waste loads from hydrochloric acid manufacture are presented below. Some of these are markedly dependent on conditions, with most of the wastes being produced during startups. There are no water-borne wastes during periods of normal operation.

Waste Products	Process Source	Amount of Product
1. Chlorine*	Burner Run - Chlorine-rich	Startup - 100 kg/kkg (200 lb/ton) avg. 5-200 range (10-400) Operation - 5 kg/kkg (10 lb/ton) avg. 0-10 range (0-20) Shutdown - no waste
2. HCl**	-	Startup - 4.5 kg/day (9 lb/ton) Operation - none Shutdown - none

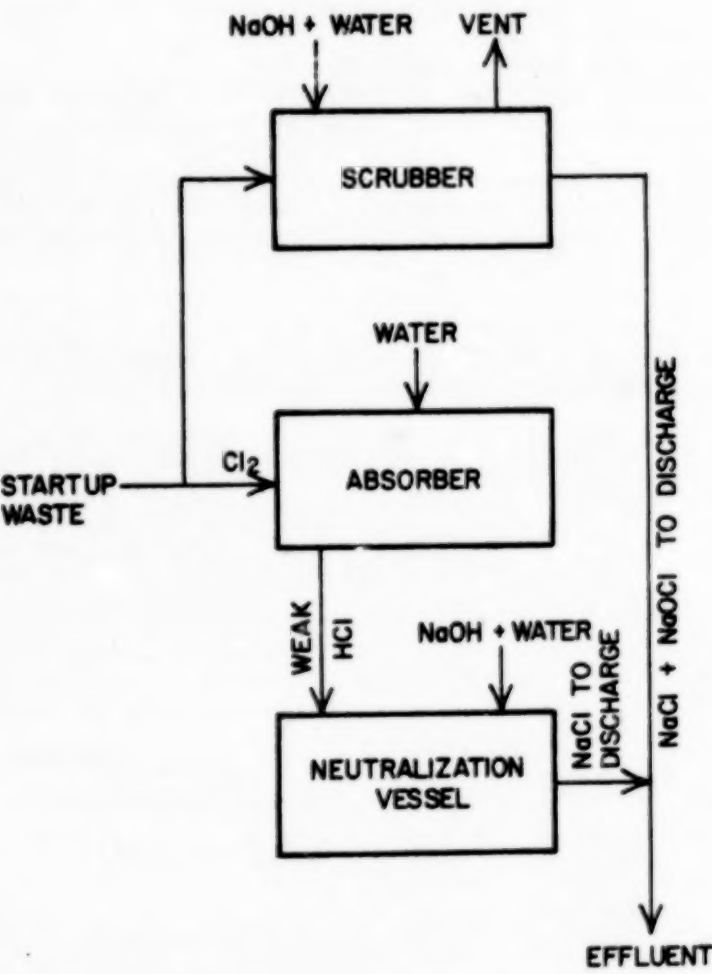


FIGURE 42  
STARTUP WASTE TREATMENT SYSTEM  
AT PLANT 121

3. NaOH\*\*\* Neutralization Startup - depends on HCl and Cl<sub>2</sub> to be neutralized  
 reaction products Operation - none  
 (NaCl and NaOCl) Shutdown - none

\*Emerges in vent gas during normal operation, neutralized during startup by NaOH.  
 \*\*All neutralized during startup.  
 \*\*\*Caustic (NaOH) used has 12 percent NaCl present and is cell liquor from chlorine plant also in the complex.  
 All waste water treatment is performed during startup of the facility. During normal operation, there are no water-borne wastes to be treated. Water use at the facility is listed below:

#### A. Input

Type	Quantity		Comments on Content
	cu m/day	l/kg	
Lake	5,680 (150,000 gpd)	15,650 (3,750 gal/ton)	TDS-300 mg/l, SS-10 mg/l, Cl-65 mg/l, SO <sub>4</sub> -34 mg/l, CaCO <sub>3</sub> -200 mg/l, Ca(HCO <sub>3</sub> ) <sub>2</sub> -2-250 mg/l.
Well	1,135 (30,000 gpd)	3,130 (750 gal/ton)	Same as lake water except lower in sulfate, low SS (less than 10 mg/l).

#### B. Water Use

Type	Quantity		Percent Recycled
	cu m/day	l/kg	
Cooling*	1,135 (30,000 gpd)	3,130 (750 gal/ton)	0
Process	760 (20,000 gpd)	2,085 (500 gal/ton)	0 (Leaves as part of product)
Disposal from neutralization tank**	4,545 (120,000 gpd)	12,520 (300 gal/ton)	0
Miscellaneous	380 (10,000 gpd)	1,040 (250 gal/ton)	0

\*Phosphate treatment used for this water. About 0.5 mg/l excess phosphate is employed.

\*\*For safety purposes, continuous water flow is maintained into the neutralization tank even during normal process operation when no effluent or NaOH are introduced.

The effluents from the process streams before sewer at plant 121 are listed below.

Waste Stream	cu m/day	l/kg
1. Neutralizing Reactor	4,355 (115,000 gpd)	12,000 (2,875 gal/ton)
2. Neutralizing Siphon Tank*	190 (5,000 gpd)	520 (125 gal/ton)
3. Test Sink and Washdown	380 (10,000 gpd)	1,040 (250 gal/ton)
4. Cooling Water	1,135 (30,000 gpd)	3,130 (750 gal/ton)

\*Siphon Tank is 26,500 l and has less than 4 l/day drainage. It is operated batchwise with excess caustic always present. When the alkali content has been neutralized, it is disposed of.

After treatment, these streams are fed to a common equalization pond for pH adjustment and suspended solids removal prior to discharge. Effluent after this treatment (for the total complex) contains less than 10 mg/l of suspended solids and 2588 mg/l chlorides and sulfates, mostly from other processes.

The plant effluent characteristics are given below. There are no wastes during normal operation. All of the wastes arise from startup operations. In addition, there is an air-borne chlorine vent gas waste as noted earlier.

Parameter	Stream No. 1		Stream No. 2		Stream No. 3		Stream No. 4
	Operation/Startup	Operation/Startup	Operation/Startup	Operation/Startup	Operation/Startup	Operation/Startup	
Total Suspended Solids	10*mg/l	10 mg/l	No Effluent		Batch for a number of processes; 90-180 kg of Cl <sub>2</sub> neutralized per month and disposed of in this stream		Same as lake water
Total Dissolved Solids	300*mg/l	40,000-50,000					
BCD	**	10 mg/l					
CCD	**	**					
pH	6.5-10.0 9 avg.	6.5-10.0 9 avg.					

\*Same as lake water

\*\*Undetectable



All of the chlorine-burning HCl plants are located within chlor-alkali complexes. At present, there are four such facilities.

The 121 plant was sampled because of two considerations: 1) Unlike the other facilities, hydrochloric acid wastes are easily segregable. At other plants these wastes are mixed with chlor-alkali wastes before treatment; and 2) Unlike some other facilities, there are no hydrochloric acid wastes during normal operations.

This facility could be further improved by: (1) More efficient scrubbing of process tail gases to remove chlorine and use of the resulting chloride/hydrochloric solutions elsewhere in the facility; and (2) Reuse of the sodium chloride formed by acid neutralization.

#### Hydrofluoric Acid

Hydrofluoric acid is manufactured by reaction of sulfuric acid with fluorspar ore (mainly calcium fluoride). The reaction mixture is heated and the hydrofluoric acid leaves the furnace as a gas, which is cooled, condensed and sent to a purification unit. There the crude hydrofluoric acid is redistilled and either absorbed in water to yield aqueous hydrofluoric acid or compressed and bottled for sale as anhydrous hydrofluoric acid.

At an exemplary plant (plant 152), the calcium sulfate byproduct from the reactor is slurried with water and sent to waste treatment. Also, all tail gases are scrubbed and the scrubber water is sent to the waste abatement system. Figure 43 shows a detailed process diagram for the exemplary facility, and Figure 44 shows the waste water recycling system in use at this plant.

The waste products from hydrofluoric acid manufacture are shown below. Wastes consist of materials from the furnaces, which include calcium sulfate, calcium fluoride and sulfuric acid, plus fluoride-containing scrubber wastes.

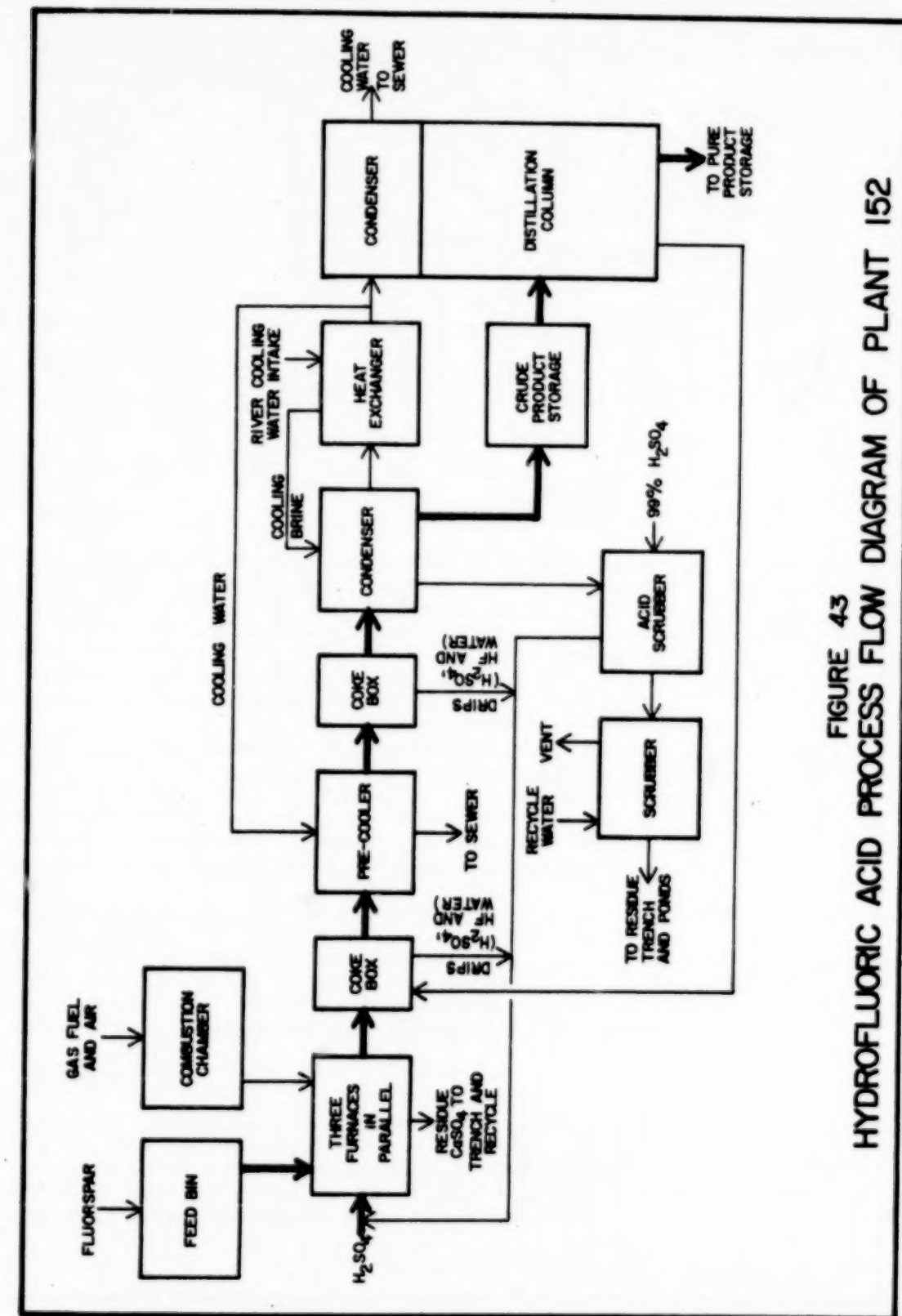


FIGURE 43  
HYDROFLUORIC ACID PROCESS FLOW DIAGRAM OF PLANT 152

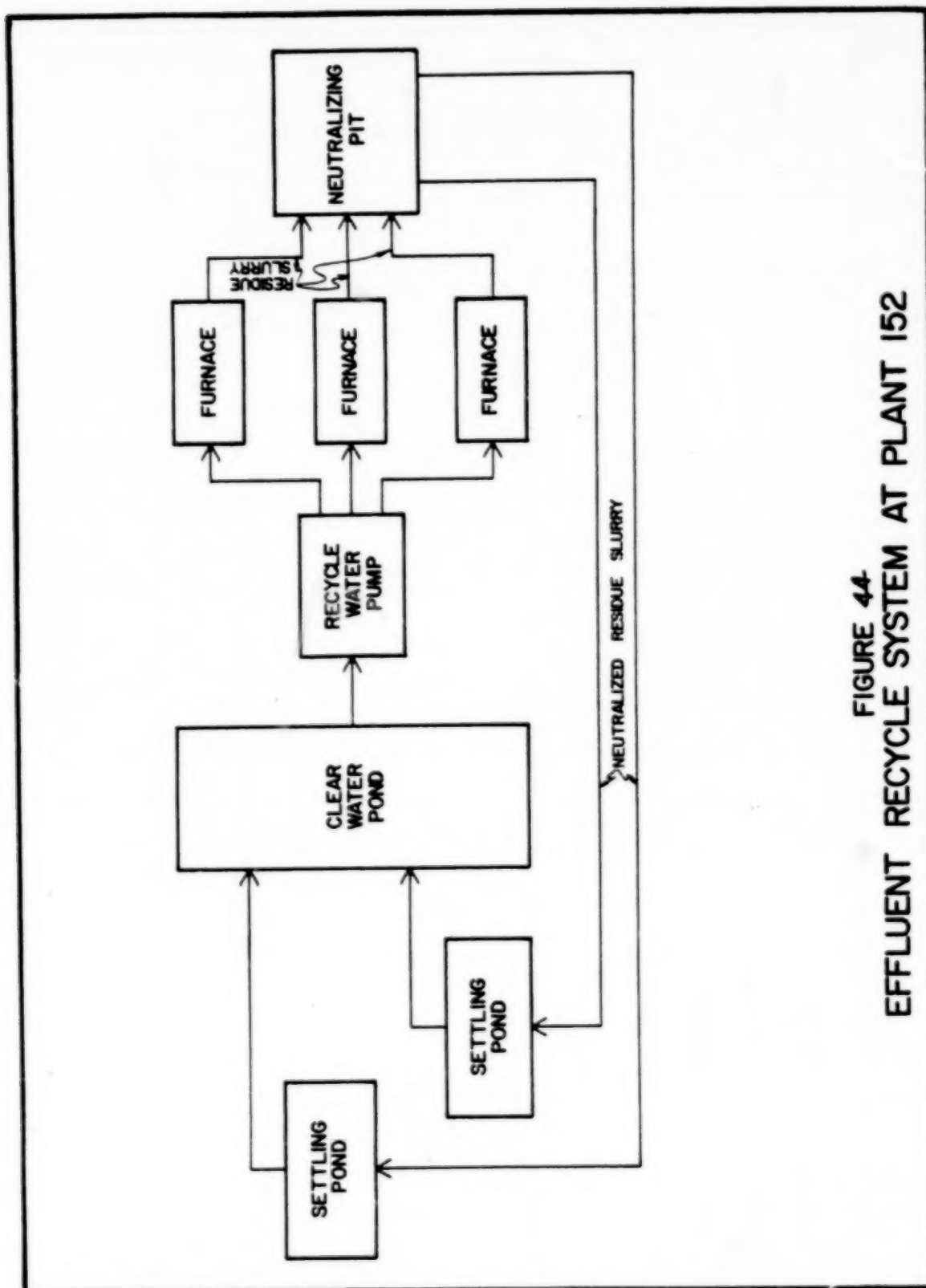


FIGURE 44  
EFFLUENT RECYCLE SYSTEM AT PLANT 152

Waste Product	Process Source	Avg. kg/kg (lb/ton) of Product
1. $\text{CaSO}_4$	Kiln (reactor)	3,620 (7,240)
2. $\text{H}_2\text{SO}_4$	Kiln (reactor)	110 (220)
3. $\text{CaF}_2$	Kiln (reactor)	63 (126)
4. $\text{HF}$	Kiln (reactor)	1.5 (3)
5. $\text{H}_2\text{SiF}_6$	Scrubber	12.5 (25)
6. $\text{SiO}_2$	Kiln (reactor)	12.5 (25)
7. $\text{SO}_2$	Scrubber	5 (10)
8. $\text{HF}$	Scrubber	1 (2)

The water use within plant 152 is shown below.

Type	Total Quantity		Recycled
	cu m/day (gpd)	l/kg (gal/ton)	
Cooling (river water)	3,270 (864,000)	90,140 (21,600)	0 percent
Slurry and Scrubber	3,270 (864,000)	90,140 (21,600)	100 percent

All process and scrubber waste waters are recycled in the exemplary plant. The waters used to slurry and remove the calcium sulfate from the furnaces and scrubber waters are fed to a pond system after being treated with caustic or soda ash and lime to precipitate fluorides and adjust the pH. In the pond system, the insolubles are settled out and the waters are then reused in the process as shown in Figure 44.

Only cooling water is discharged from this facility. Table 11 shows the compositions of process waters before and after neutralization and of the river intake water which is essentially the same as the cooling water effluent. Low fluoride levels are easily maintained because of segregation of discharged cooling waters from the process water.

Verification measurements, shown for the plant intake water and the outflow of cooling water, are given in Table 12. The similarity of the intake and cooling water discharge verifies that there is no process water leakage into the cooling stream, and, therefore, there is no process water discharge from this exemplary hydrofluoric acid manufacturing plant.

#### Hydrogen Peroxide

Hydrogen peroxide is manufactured by three different processes: (1) An electrolytic process; (2) An organic process involving the oxidation and reduction of anthraquinone; and (3) A by-product of acetone manufacture from isopropyl alcohol. In this study, only the first two processes were considered.

TABLE 11. Intake Water and Raw Waste Composition Data at Plant 152\*

Parameters		Units	Raw Waste Into Treatment	Recycle Water From Treatment	Intake River Water
Aluminum	Al	µg/l	7400	2200	2600
Beryllium	Be	"	66	64	20
Calcium	Ca	mg/l	640	450	12.2
Cadmium	Cd	µg/l	16	12	2
Cobalt	Co	"	300	280	26
Chromium	Cr	"	46	22	4
Copper	Cu	"	44	28	4
Iron	Fe	"	3100	780	1060
Magnesium	Mg	mg/l	6.0	6.4	3.2
Manganese	Mn	µg/l	100	106	68
Molybdenum	Mo	"	56	56	26
Nickel	Ni	"	80	68	4
Lead	Pb	"	1320	3400	820
Titanium	Ti	"	240	220	20
Zinc	Zn	"	1100	880	440
Barium	Ba	"	740	1020	1280
Potassium	K	mg/l	6.4	8.6	0.6
Sodium	Na	"	490	660	4.2
Tin	Sn	µg/l	140	140	24
Ammonia-Nitrogen	mg/l N	"	0.23	0.05	0.23
COD	02	"	13.4	-	-
Fluoride	F	"	13.0	12.5	0.2
Total Suspended Solids	"	"	16596	59	21
Total Solids	"	"	22015	3758	124
Total Vol. Solids	"	"	1220	340	58
Total Dissolved Solids	"	"	4250	3572	132
Nitrate	mg/l N	"	0.26	0.20	0.13
Nitrite	"	"	0.02	0.01	0.20
Nitrogen-Kjeldahl	"	"	0.57	0.46	0.46
Phosphate Total	mg/l P	"	1.60	0.96	0.02
Sulfate	mg/l S	"	880	767	7
Arsenic	µg/l	"	77	49	74
pH	-	"	3.86	7.22	7.17
TOC	mg/l	"	4	6	5

\*Data furnished by manufacturer

TABLE 12. Comparison of Plant Intake Water and Cooling Water Discharge at Plant 152\*

Parameter	Intake	Discharge	Units
Flow	Not Measured	3,270 (864,000)	cu m/day (GPD)
Temperature	Not Measured	18 (64)	°C (°F)
Color (Apparent)	50	50	Units APHA
Turbidity	19	19	FTU
Conductivity	65	65	mg/l NaCl
	135	135	micromhos/cm
Suspended Solids	7	12	mg/l
pH	7.40	7.50	-
Acidity: Total	0	0	mg/l CaCO <sub>3</sub>
Free	0	0	mg/l CaCO <sub>3</sub>
Alkalinity (Total)	0	0	mg/l CaCO <sub>3</sub>
	P	0	mg/l CaCO <sub>3</sub>
	T	30	mg/l CaCO <sub>3</sub>
Hardness: Total	50	50	mg/l CaCO <sub>3</sub>
Halogens: Chlorine	0	0	mg/l Cl <sub>2</sub>
Fluoride	0.2	0.2	mg/l F-
Sulfate	25	22	mg/l SO <sub>4</sub> -2
Nitrogen (Total)	0.20	0.14	mg/l N
Heavy Metals:			
Iron	0.25	0.25	mg/l Fe
Chromate (Cr+6)	0.02	0.02	mg/l Cr+6
Oxygen (Dissolved)	11	10.4	mg/l O <sub>2</sub>
COD	25	0	mg/l

\*Data from verification sampling



a) Organic process

In the organic process, anthraquinone (or an alkylanthraquinone) in an organic solvent is catalytically hydrogenated to yield a hydroanthraquinone. This material is then oxidized with oxygen or air back to anthraquinone, with hydrogen peroxide being produced as a by-product. The peroxide is water-extracted from the reaction medium, and the organic solvent and anthraquinone are recycled. The recovered peroxide is then purified and shipped. Figure 45 shows a specific flowsheet for plant 069, including part of the waste abatement program.

Waste Products	Process Source	Operation Avg. Range kg/kkg (lb/ton)
Sulfuric Acid	Ion Exchange Units	12.5-15 (25-30)
Trace Organics	Contact Cooling	0.17-0.35 (0.34-0.70)
Hydrogen Peroxide	Purification Washings	20-25 (40-50)

The process runs continuously, except for shut-down approximately 10 days/year. Total discharge will normally be no higher during start-up and shut-down periods than under operation at capacity.

Well water at 312 cu m/kkg of product (74,500 gal/ton) having the following composition in the water input at plant 069.

Total Solids	110-125 mg/l
Carbon Dioxide	30-60 mg/l
Total Hardness	80-100 mg/l
Fe	1-3 mg/l
Cu	0.03-0.06 mg/l
Zn	0.02 mg/l
Sulfate	2-7 mg/l
Alkalinity (CaCO <sub>3</sub> )	70-110 mg/l

Water Usage

Type	cu m/kkg (gal/ton)	% Recycled
Cooling	365 (87,200)	25 percent recycled 35 percent of remainder used twice
Process	16 (3,800)	----

Most of the water is used for cooling, and a relatively large fraction of this water is recycled.

The data below describes the treatment of the waste stream emerging from the peroxide plant. Peroxide is decomposed by iron filings, and organic solvent losses are minimized by a skimming operation:

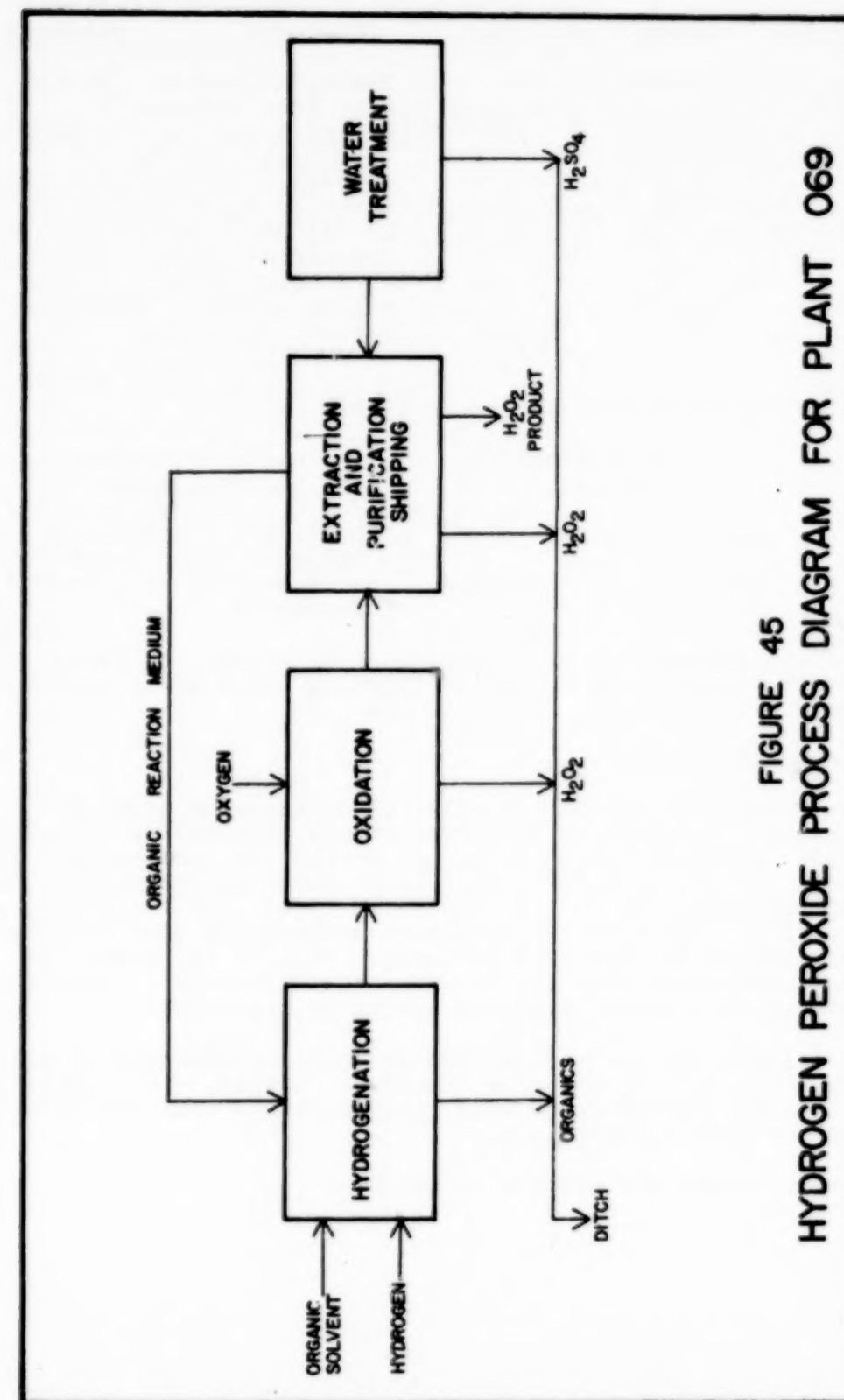


FIGURE 45  
HYDROGEN PEROXIDE PROCESS DIAGRAM FOR PLANT 069

Waste Stream	Source	cu m/kg (gal/ton)	Treatment	Final Disposal
Process Effluent	Process	294 (70,200)	1. Peroxide reacted with iron filings 2. Skimmers used to trap organics for recovery 3. Waste sulfuric acid is collected and discharged at a controlled rate 4. Solids (alumina & carbon) are hauled to landfill	River

The effectiveness of the treatments in use is:

Method	Qualitative Rating	Waste Reduction Accomplished
Reduction	Generally satisfactory	80 percent reduction of per- oxide to water and oxygen
Skimming	Generally satisfactory	60-70 percent of organics recovered

The effluent composition after treatment is given in Table 13. The wastes consist of unreacted peroxide and a small amount of organics and sulfates.

#### b) Electrolytic process

In the electrolytic process, a solution of ammonium bisulfate is electrolyzed. Hydrogen is liberated at the cathodes of the cells used, and ammonium persulfate is formed at the anode. The persulfate is then hydrolyzed to yield ammonium bisulfate and hydrogen peroxide which is separated from the solution by fractionation. The ammonium bisulfate solution is then recycled, and the peroxide is recovered for sale. The only waste is a stream of condensate from the fractionation condenser. Figure 46 shows the process waste treatment system at plant 100.

Table 14 lists the raw wastes from peroxide manufacture at plant 100. These consist of ammonium bisulfate losses, ion exchange losses, boiler blowdowns and some cyanide wastes from the special batteries used in electrolysis.

Plant water intake and use are as follows:

TABLE 13. Plant 069 Process Water Effluent After Treatment

Parameter*	Plant Data		Verification Sample	
	Average	Range	Verification Measurement	Plant 069 Measurement
Total Suspended Solids	-	15-20	9	9
Total Dissolved Solids	-	310-330	98	117
BOD	-	6-7	-	-
COD	40	-	50	33
pH	-	6-9	6.4	6.6
Temperature	30°C	-	27°C	-
T.O.C.	-	5-15	-	-
Hydrogen Peroxide	-	60-80	-	37.8
Turbidity (Jackson Units)	25	-	12	25
Color (APHA Units)	-	20-20	50	10
Acidity (Free)	-	40-50	-	46
Acidity (Total)	0	-	-	-
Alkalinity (Total)	-	150-195	61	-
Hardness (Total)	-	90-105	92	-
Chloride	2	-	5	7
Sulfate	-	40-75	43	52
Iron	-	2-3.5	1.6	0.26
Copper	-	0.08-0.09	-	-
Flow	25,000 cu m/day (6.6 MGD)	-	26,000 cu m/day (7.1 MGD)	-

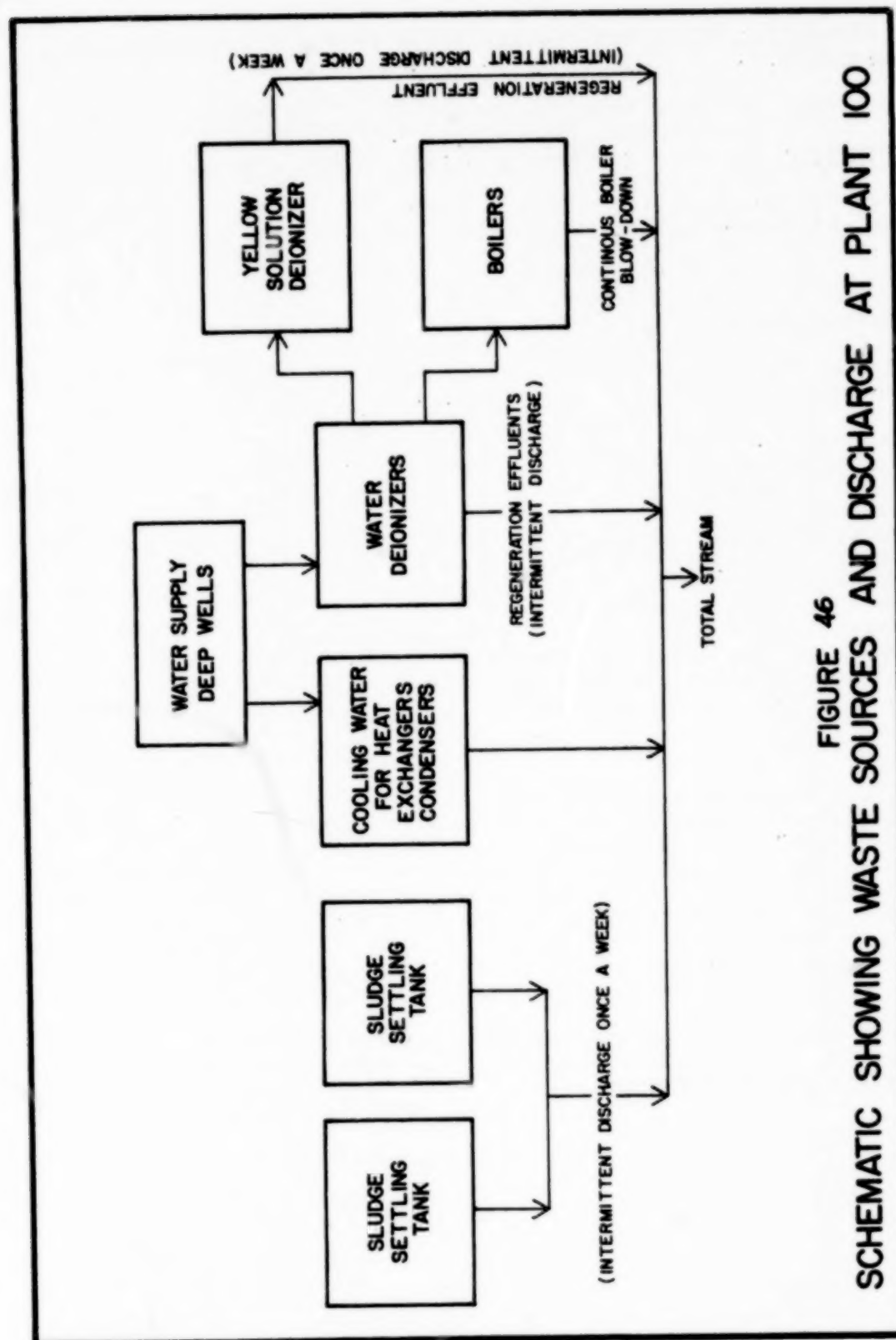


TABLE 14. Raw Waste Loads at Plant 100

Waste Product	Process Source	kg/kg of Peroxide (lb/ton)	
		Operation	Startup Shutdown
1. Blue prussiate sludge	Purif.	0.18(0.36)	No significant difference during start-up & shutdown periods. Plant runs continuously; shuts down once per year.
2. Gray sludge	Battery rebuild	(5 times per year)	
3. Ion Exchange sludge	Deionizer regen.	---	
4. $H_2SO_4$	Plant solution loss	0.0018(0.0036)	No significant difference during start-up & shutdown periods. Plant runs continuously; shuts down once per year.
5. $(NH_4)_2SO_4$	Plant solution loss	0.012(0.024)	
6. Water flow	Cooling	2000-2900 (4000-58000)	
7. HCl	Deionizer regen.	1.3(2.6)	No significant difference during start-up & shutdown periods. Plant runs continuously; shuts down once per year.
8. NaOH	Deionizer regen.	0.33(0.66)	
9. Steam condensate	Boiler blowdown	581(1162)	

Comments:  $H_2SO_4$  and  $(NH_4)_2SO_4$  are used to replenish plant solution.  $Na_4Fe(CN)_6$  is converted to  $(NH_4)_4Fe(CN)_6$  through ion exchange (yellow solution).  $NH_4SCN$  is oxidized in the batteries and is used for better current efficiency. HCl and NaOH are used for regeneration of demineralized water ion exchange resins.



<u>Water</u>	<u>Flow, cu m/day</u> <u>(mgd)</u>	<u>Amount, l/kg</u> <u>(gal/ton)</u>	<u>Use</u>
Municipal	7.2 (0.0019)	601 (114)	Drinking, Washing, Sanitary
Well	41,600 (11.0)	3,480,000	76 cu m/day (0.002 mgd) demineralized for process water, rest used as cooling

Of the 76 cu m/day of process water, 31 percent is used in the product. Recycle flow of process water is 132 cu m/day and recycle flow of steam is 305 cu m/day (liquid basis). About 26.5 cu m/day is boiler blowdown. None of the cooling water is recycled. Table 15 lists the various plant effluent streams, their sources, flows and treatments. Treatments consist of ion exchange for pH control and recovery of some process materials, and recovery of platinum in the waste streams. After this, wastes are discharged.

Performance information on the pH control and ion exchange technology used for waste abatement in this plant is:

<u>Method</u>	<u>Qualitative</u> <u>Rating</u>	<u>Waste Reduction</u> <u>Accomplished</u>
1. pH Control	Good	99+ percent
2. Process change	Excellent	CN- load reduced 98 percent - Additional concentration to discharge stream less than 0.01 mg/l
3. Monitoring	Good	Reduces unknown discharges and allows quick operation response.

Table 16 lists the compositions of the various effluent streams after treatment. These streams are mixed prior to discharge. Table 17 shows an analysis of the intake water and final effluent after mixing. Only very small amounts of materials are introduced into the waters used, and cyanides in the effluent are negligible.

#### Nitric Acid

Nitric acid is manufactured from ammonia by a catalytic oxidation process. Ammonia is first catalytically oxidized to nitric oxide, which is then further oxidized to nitrogen dioxide. The nitrogen dioxide is then reacted with water under pressure to yield nitric acid. Plant 114 manufactures only commercial 63

TABLE 15. Effluent Treatment Data for Plant 100

#### A. Water Streams

<u>Stream No.</u>	<u>Source</u>	<u>1/day</u> <u>(MGD)</u>	<u>1/kg</u> <u>(gal/ton)</u>
1. Low Exchange Regenerant	Demineralizer	3,790(1,000)	317(76)
2. Blue Prussiate Supernatant (filter back- wash)	Filters	568(150) *	47.6(11.4)
3. Yellow Solution	Ion Exchange	568(150) *	47.6(11.4)
4. Boiler Blowdown	Boilers	26,500(7,000)	2,210(530)

#### B. Treatments

<u>Stream No.</u> <u>(same as above)</u>	<u>Treatment Method</u>	<u>Final</u> <u>Disposal</u> <u>System</u>
1	Anion and cation regener- ants are mixed to control pH and slowly released.	Plant effluent
2	Settled for platinum recov- ery, siphoned and filtered**.	Plant effluent
3	Backwash recycled to pro- cess and regenerant is discharged.	Plant effluent
4	Dilution	Plant effluent

\*These operations are batch carried out an average of once per week.

\*\*Sludges recovered here are sent to refiners for recovery of platinum values.

TABLE 16. Composition of Plant 100 Effluent Streams After Treatment\*

Constituents	No. 1 Stream	No. 2 Stream	No. 3 Stream	No. 4 Stream
Total Suspended Solids	1856 as CaCO <sub>3</sub> equiv. during regeneration	--	0	--
Total Dissolved Solids	Comparable to raw water	200-400	40,000	1,000
BOD	Same as raw water	--	--	--
COD	Same as raw water	--	--	--
pH	6.5-8.5	4	7	8
Temperature, °C	17	18	18	--
Conductivity micromhos/cm	7160	--	--	--
Alkalinity	--	--	--	400
Free Cyanide	--	<2	<2	0
Phosphate	--	--	--	30
Chloride	--	--	--	20-30 (as NaCl)

\*all units mg/l unless otherwise specified.

TABLE 17. Plant 100 Water Intake and Final Effluent Verification Measurements

Parameter*	Well Water	Outfall
Conductivity, micromhos/cm	120 (as NaCl) 240	120 (as NaCl) --
Color	0	0
Turbidity	0	0
SS	0	0
pH	6.88	7.04
Sulphate	18	21
Nitrate	3.3	2.3
Phosphate	0.35	0.36
Iron	0.02	0.01
Chloride	6.5	7.5
Hardness (Ca)	65	70
Total Hardness	95	90

\*mg/l unless otherwise specified.

percent nitric acid. Fuming (i.e., more than 70 percent) nitric acid and nitrogen pentoxide are made only at a few facilities and are not covered in this report. The flow diagram for plant 114 is given in Figure 47.

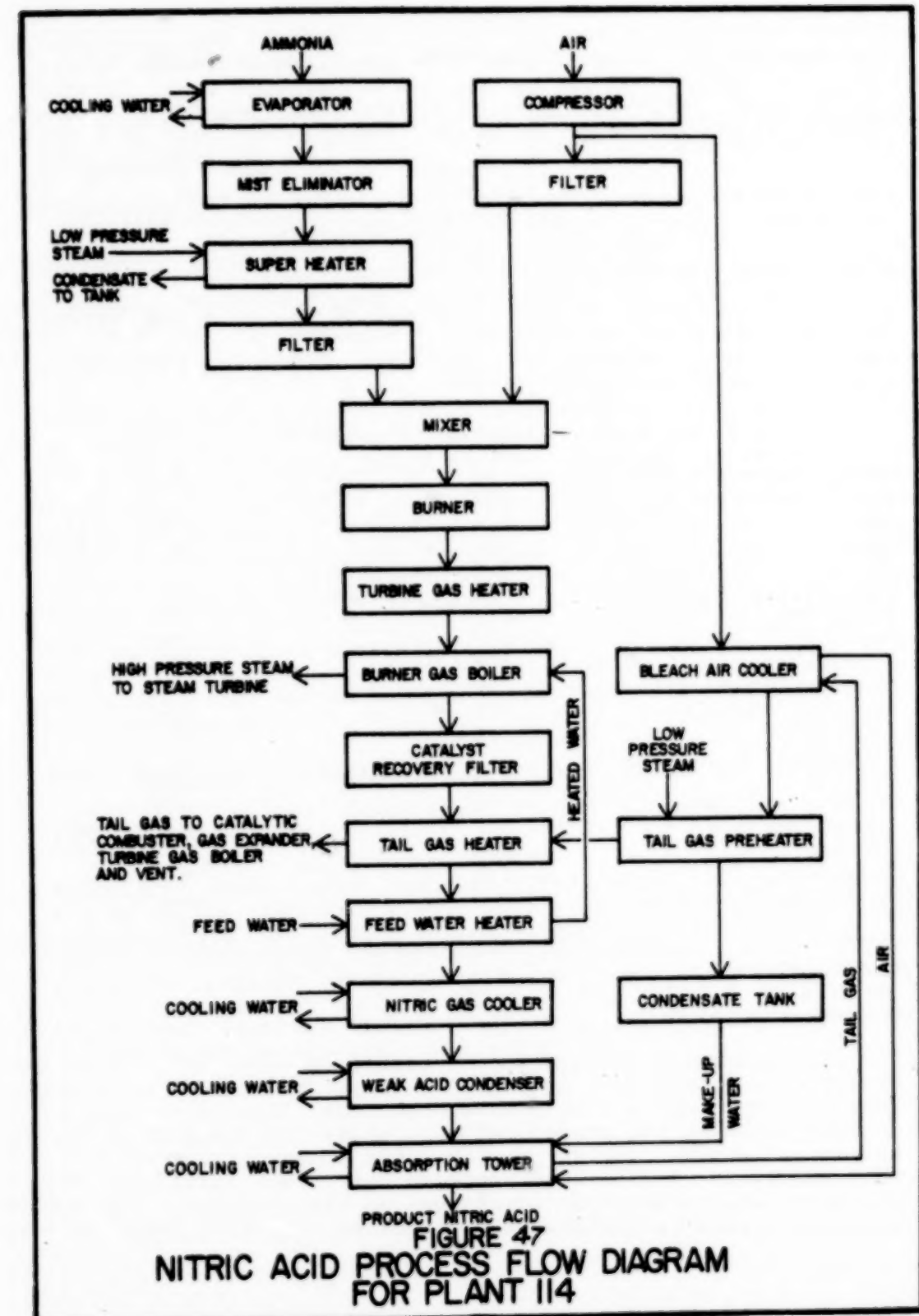
The raw waste load from nitric acid production at Plant 114 is listed below. The waste values are not affected by startup or shutdown. There are no nitrates in the waste. All weak nitric acid lost in the manufacturing process is recycled to the process at this facility. The wastes consist only of water treatment chemicals used for the cooling water.

Waste Products	Process Source	Avg. kg/kg HNO <sub>3</sub> (lb/ton)
1. Lime	Boiler Feedwater	0.47 (0.94)
2. Calcium and Magnesium Carbonates	Boiler Feedwater	0.6 (1.2)
3. Disodium Phosphate	Boiler	0.0016 (0.0032)
4. Sodium Sulfate	Boiler	0.0008 (0.0016)
5. Sulfuric Acid	Cooling Tower	0.0016 (0.0032)
6. Chlorine	Cooling Water Treatment	1.0 (2.0)

Plant water use is shown below and describes the large amount of water and weak acid recycling at the plant. Only cooling water is discharged, and this waste stream is currently untreated.

A. Water Inputs		Quantity	
Types		cu m/day	l/kg
Well		3,815	13,150
		(1,008,000 gpd)	(3,150 gal/ton)
B. Water Use		Quantity	
		cu m/day	l/kg
Cooling		31,000	106,800
		(8,000,000 gpd)	(25,000 gal/ton)
Process stream		775	2,670
		(200,000 gpd)	(6,250 gal/ton)

The plant effluent streams are shown below. Wastes discharged are only water treatment chemicals.





<u>Sources</u>	<u>cu m/day</u>	<u>l/kkg</u>
Boiler Feedwater	5	16
Treatment	(1,250 gpd)	(3.9 gal/ton)
Boiler Blowdowns	30	85
	(7,800 gpd)	(24.4 gal/ton)
Cooling Water	3600	1240
Blowdowns	(95,000 gpd)	(297.0 gal/ton)

(All streams tie into common effluent header before discharge)

Because of recycling of some water and of all nitrogen-containing streams, this plant is exemplary. However, as in many other cases, cooling waters are untreated prior to discharge. The plant effluents are listed below.

	<u>Average</u>	<u>Range</u>	<u>Units</u>
Total Suspended Solids	80	50-100	mg/l
Total Dissolved Solids	239	200-250	mg/l
BOD	5	-	mg/l (O2)
CCD	10	-	mg/l (O2)
pH	7.8	7.5-8.5	-
Temperature	25	24-27	°C
Turbidity	125	-	JTU
Color	330	-	PTCO
Conductivity	500	-	mhos
Alkalinity (Total)	300	-	mg/l
Hardness (Total)	300	-	mg/l
Chloride	18	-	mg/l
Fluoride	0.2	-	mg/l
Sulfite	0.2	-	mg/l
Sulfate	60	-	mg/l
Phosphates	0.4	-	mg/l
Nitrate	0.2	-	mg/l
Iron	7.5	-	mg/l
Manganese	0.2	-	mg/l

A plant visit verified that only cooling water is discharged from plant 114.

#### Potassium Metal

For the commercial preparation of potassium metal (K), potassium chloride is melted in a gas-fired melt pot and fed to an exchange column. The molten potassium chloride flows down over steel Raschig rings in the packed column, where it is contacted by ascending sodium vapors coming from a gas-fired reboiler. An equilibrium is established between the two, yielding sodium chloride and elemental potassium as the products. The sodium chloride formed is continuously withdrawn at the base of the

apparatus and is normally sold. The column operating conditions may be varied to yield either pure potassium metal as an overhead product or to vaporize sodium along with the potassium to produce sodium potassium (NaK) alloys of varying compositions. Potassium metal of over 99.5 percent purity can be continuously produced by this process.

Production of potassium in the United States was about 90 kkg (100 ton) in 1972, essentially all of it originating from one facility - plant 045. Contacts with this manufacturer have revealed that the process diagram accurately describes their process. No process water is used and there are no waterborne effluents.

#### Potassium Dichromate

Potassium dichromate is prepared by reaction of potassium chloride with sodium dichromate. Potassium chloride is added to the dichromate solution, which is then pH-adjusted, saturated, filtered and vacuum cooled to precipitate crystalline potassium dichromate. The product is recovered by centrifugation, dried, sized and packaged. The mother liquor from the product centrifuge is then concentrated to precipitate sodium chloride which is removed as a solid waste from a salt centrifuge. The process liquid is recycled back to the initial reaction tank.

The raw wastes from potassium dichromate manufacture are listed below. These are crystalline sodium chloride and filter aids which are solid wastes and are hauled away for landfill disposal by a contractor.

<u>Waste Products</u>	<u>Process Source</u>	<u>kg/kkg of Product (lb/ton)</u>
NaCl	Centrifuge	400 (800)
Filter aid	Filter	0.85 (1.7)

Exemplary plant water usage is given below. All process waters are recycled. The only wastes currently discharged emanate from contamination of once-through cooling water used on the barometric condensers on the product crystallizer. Plant 002 has plans to replace the barometric condensers with heat exchangers using non-contact cooling water. This should eliminate the hexavalent chromium waste completely. With this change, no process waste waters will be discharged.

#### A. Water Inputs to Plant

Type	Quantity		Comments
	cu m/day	l/kgg	
River	1,325 (350,000 gpd)	97,200 (23,300 gal/ton)	Untreated except for macrofiltration
Municipal	245 (65,000 gpd)	18,100 (4,330 gal/ton)	Untreated

#### B. Water Usage

Type	Quantity		Recycle
	cu m/day	l/kgg	
Cooling	1,325 (350,000 gpd)	97,200 (23,300 gal/ton)	0
Process (makeup)	245 (65,000 gpd)	18,100 (4,330 gal/ton)	100

Presently, the only effluent from this plant is cooling water, possibly contaminated with hexavalent chromium in the barometric condenser. Replacement of the condenser with a non-contact heat exchanger will eliminate cooling water contamination, although a larger amount of water will have to be used for the less efficient non-contact heat exchanger.

#### Potassium Sulfate

The bulk of the potassium sulfate manufactured in the United States is prepared by reaction of potassium chloride with dissolved langbeinite ore (potassium sulfate-magnesium sulfate). The langbeinite ore is mined and crushed and then dissolved in water to which potassium chloride is added. Partial evaporation of the solution produces selective precipitation of potassium sulfate which is recovered by centrifugation or filtration from the brine liquor, dried and sold. The remaining brine liquor is either discharged to an evaporation pond, reused as process water or evaporated to dryness to recover magnesium chloride. The fate of the brine liquor is determined by the saleability of the magnesium chloride by-product (depending on ore quality) and the cost of water to the plant. A diagram for the process used at plant 118 is given in Figure 48.

The table below presents a list of the raw wastes expected for potassium sulfate manufacture:

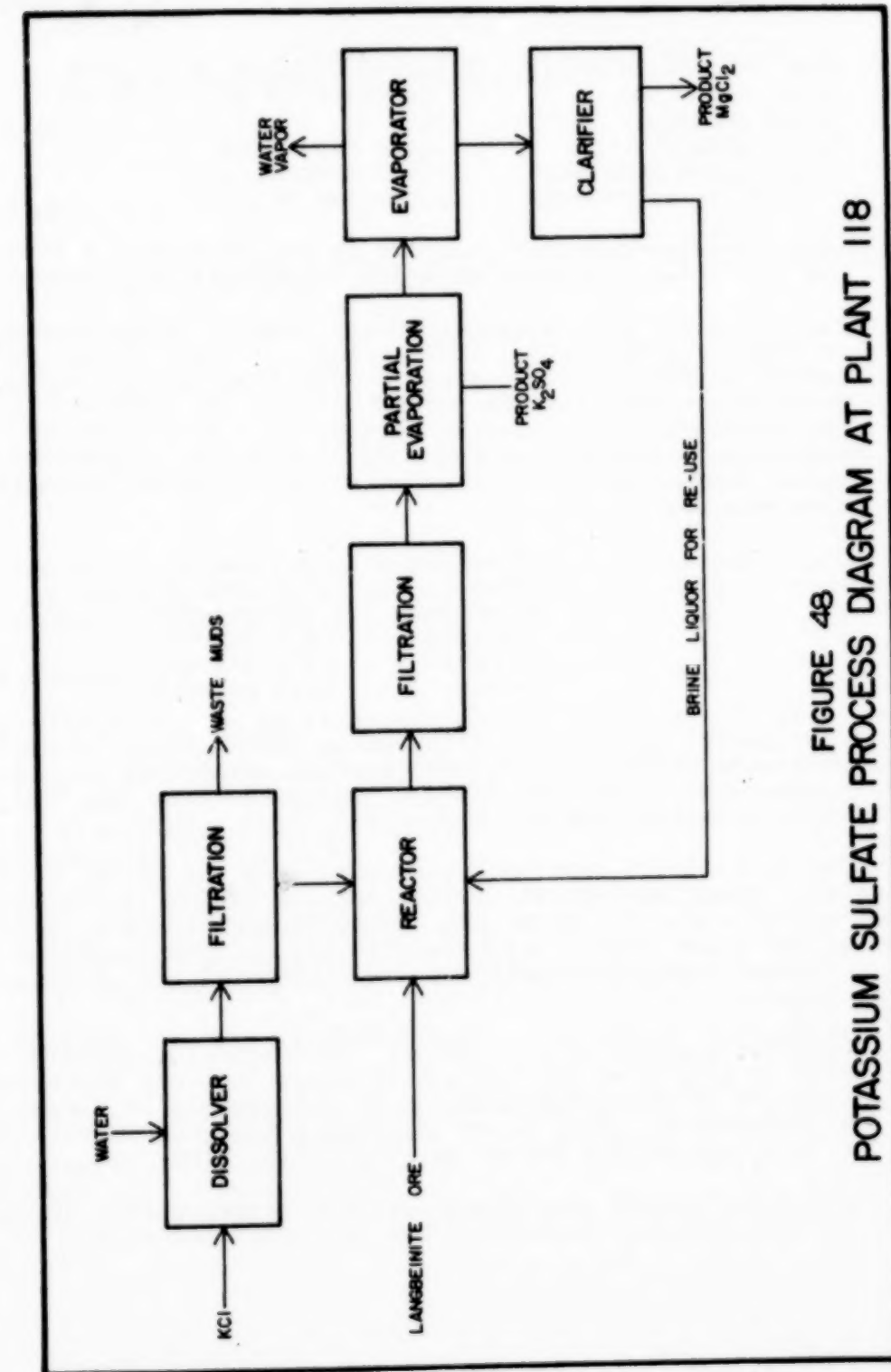


FIGURE 48  
POTASSIUM SULFATE PROCESS DIAGRAM AT PLANT 118

Waste Product	Process Source	kg/kkg of Product (lb/ton)	
		Average	Range
Muds, (silica, alumina, clay and other insolubles)	Dissolution of langbeinite ore	15-30 (30-60)	-
Brine liquor (Saturated magnesium chloride solution)	Liquor remaining after removal of potassium sulfate	-	0-2000*

\*Part of the magnesium chloride is recovered for sale and part of the remaining brine solution is recycled for process water.

The high value corresponds to the case of no recycle or recovery of magnesium chloride. These brines contain about 33 percent solids. The wastes consist of muds from the ore dissolution and waste magnesium chloride brines and are not affected by startup or shutdown. The latter brine can sometimes be used for magnesium chloride production if high grade langbeinite ore is used. Composition of the brine solutions after potassium sulfate recovery is:

Potassium	3.2 percent
Sodium	1.3 percent
Magnesium	5.7 percent
Chloride	18.5 percent
Sulfate	4.9 percent
Water	66.7 percent

The amount of brine produced is about 650 kg of solids/kkg of potassium sulfate (1300 lb/ton) after evaporation. For higher grade ores, the sodium content is lower. The data presented above were supplied by plant 118.

The muds listed above are separated from the brine solutions at this exemplary plant by filtration after dissolution of the langbeinite ore. These are recovered and disposed of as landfill on the plant site. The brine wastes, containing mostly magnesium chloride, are either disposed of or treated in three different manners:

1. Evaporation with recovery of magnesium chloride for sale. This is practiced only when high grade ores are processed.
2. Reuse of the brine solution in the process in place of using process water. This is normally done to a considerable extent.
3. Disposal of the brines in evaporation pits.

At plant 118, all three of the above options are practiced, depending on the quality of the ore being processed.

Water use at plant 118 is described below:

#### Water Inputs:

Type	Quantity		Water Purity
	cu m/day (mgd)	l/kkg (gal/ton)	
Well Water	3,790 (1.0)	8,360 (2,000)	40 mg/l total solids

#### Water Flows:

Type	Quantity		Percent Recycled
	cu m/day (mgd)	l/kkg (gal/ton)	
Cooling	13,600 (3.6)	30,000 (7,200)	60-70 percent (remainder evaporated)
Process	2,270 (0.6)	5,010 (1,200)	67 percent recycled, 33 percent lost either by evaporation or removal from system with product or by-product.

There are no effluent streams from the plant since much of the water is recycled. Most of the water losses occur during the process evaporation steps.

#### Sodium Bicarbonate

Sodium bicarbonate is manufactured by the reaction of soda ash and carbon dioxide in solution. The product bicarbonate is separated by thickening and centrifugation and is then dried, purified and sold. A detailed process diagram for plant 166 is given in Figure 49. This facility is located within a Solvay process complex.

A listing of raw wastes produced in bicarbonate manufacture at plant 166 is shown below. These consist of unreacted soda ash, solid sodium bicarbonate, boiler wastes and ash from power generation equipment. The ash is treated as a solid waste.

Waste Product	Process Source	kg/kkg of Product (lb/ton)	
		Average	Range
1. Na <sub>2</sub> CO <sub>3</sub>	Slurry thickener overflow	38.0 (76.0)	0-375 (0-750)
2. Ash	Power generation	17.9 (35.8)	
3. Water purif. sludge	Boiler feed water purification	0.3 (0.6)	
4. NaHCO <sub>3</sub>	Slurry thickener overflow	10.0 (20.0)	



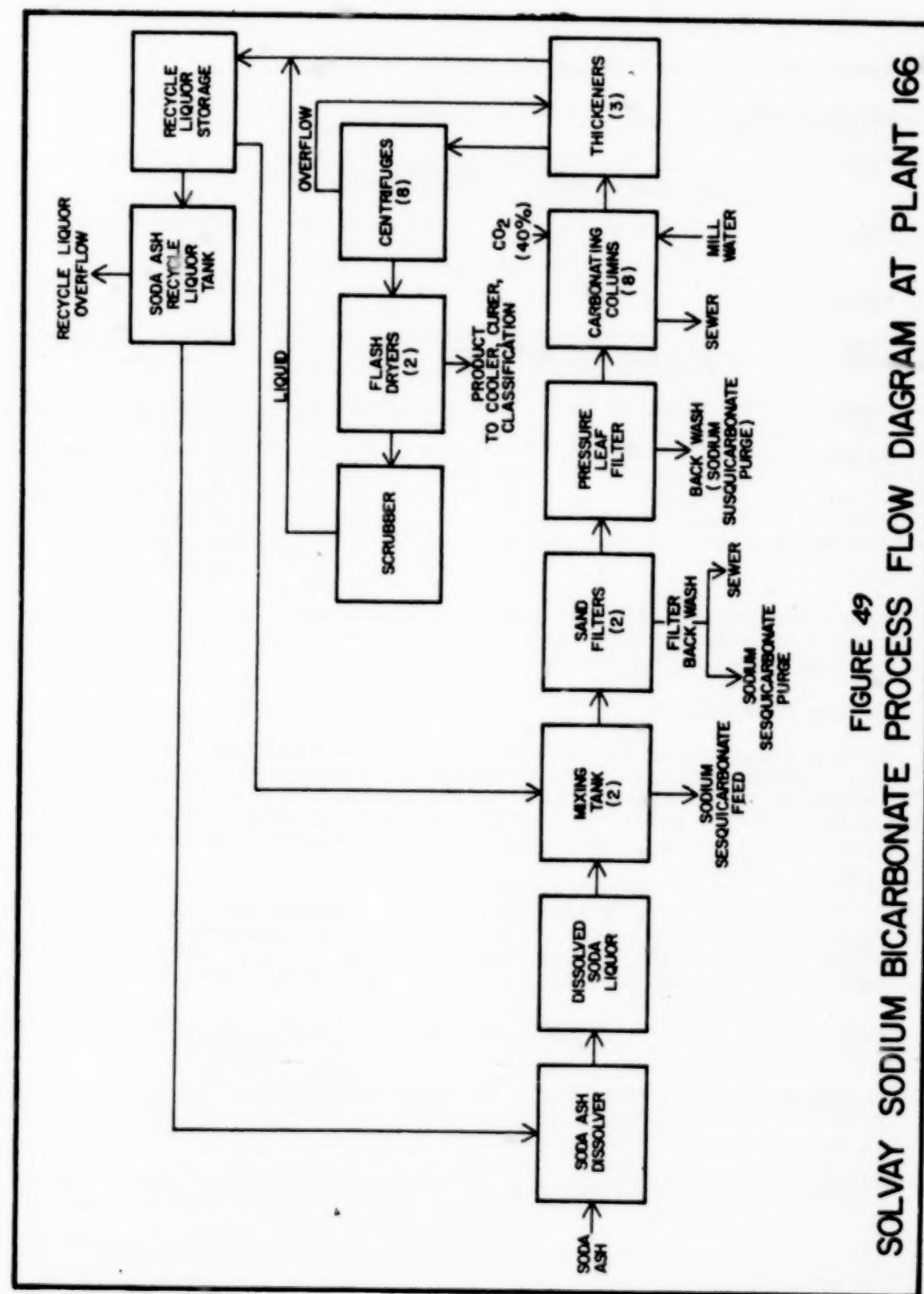


FIGURE 49  
SOLVAY SODIUM BICARBONATE PROCESS FLOW DIAGRAM AT PLANT 166

The quantity of slurry thickener overflow depends upon the operation of another plant utilizing this by-product. The overflow is not constant, and occurs only when the sister plant mentioned above cannot absorb the entire flow. Consequently, the value shown above is based on an annual average, with a wide variation in flow over the period.

The water usage at plant 166 is shown below. Most of it is used for cooling purposes.

#### Water Inputs to Plant:

Type	cu m/day (mgd)	l/kkg (gal/ton)	Treatment
Lake	1,430 (0.378)	5,430 (1,300)	Chlorinated prior to use as cooling water
Municipal	119 (0.0315)	455 (109)	

#### Water Usage:

Type	cu m/day (mgd)	l/kkg (gal/ton)	Recycled
Cooling	1,430 (0.378)	5,430 (1,300)	None
Process	119 (0.0315)	455 (109)	variable

Treatments are carried out for the two emerging waste streams. These streams are fed to settling ponds to remove suspended solids and then discharged.

Stream	Source	l/kkg (gal/ton)	Treatment	Disposal
Settling Pond Overflow	Slurry thickener	287 (69)	Settling Pond	Plant Effluent
Cooling Water (Discharge)	Various heat exchange devices found throughout plant	5,430 (1,300)	a) Containment of wastes b) Cooling water segregation c) Some water recycling d) Collection and sampling of wastes	Effluent

Individual effluents from this plant are combined with other sewer effluents. Some wastes are treated in conjunction with soda ash plant wastes. Tabulated loads are based on reasonable allocations.

The effluent from plant 166 contains 20,000 mg/l of dissolved solids (mostly dissolved carbonates), amounting to 5.75 kg/kkg of product (11.5 lb/ton). All of the bicarbonate wastes are treated

along with chlor-alkali and soda ash wastes at the 166 facility in a common treatment system prior to discharge. There are no net effluent loads to the cooling water based on average daily operation. There are no organics in the plant effluent.

Plant 166 has plans to use the weak slurry thickener overflow, which constitutes their present source of waste, as a source of liquid for the product dryer scrubber and to recycle this liquid (concentrated with respect to sodium carbonate) back to the process. These process changes will eliminate the discharge of process waste waters.

Verification measurements on the plant intake water, cooling water, and effluent are given in Table 18. The similarity of composition of plant intake and cooling water discharge verifies segregation of cooling water from process water. The process effluent measured is the effluent of the whole plant complex and hence is not indicative of that of an isolated bicarbonate unit.

#### Sodium Carbonate

Soda ash is produced by mining and by the Solvay Process. In the Solvay Process sodium chloride brine is purified to remove calcium and magnesium compounds. It is reacted with ammonia and carbon dioxide produced from limestone calcination to yield crude sodium bicarbonate which is recovered from the solutions by filtration. The bicarbonate is calcined to yield soda ash. The spent ammonia solution is reacted with slaked lime and distilled to recover ammonia values for process recycle. The calcium chloride formed as a by-product during the distillation is either discharged as a waste or recovered by evaporation. Figure 50 shows a process flowsheet for the facility at plant 166. Although all Solvay Process plants have high dissolved solids effluents, this plant is unusual in that it recovers a significant amount of an otherwise wasted by-product. Since the market for calcium chloride will not absorb the by-product generated from such recovery from all Solvay plants, this plant cannot be considered to be exemplary on this basis.

The raw waste loads for the 166 facility consist of brine purification muds, unreacted sodium chloride and the calcium chloride by-product, as follows:

TABLE 18. Plant 166 Verification Data

Parameter	Plant Intake		Bicarbonate Cooling Water	Plant Complex Effluent
	Measured	Furnished		
Flow, cu m/day (MGD)	Not measured	188,000 (49.5)*	Not Measured	17,400 (4.6)
Temperature, °C	11.2	-	Not Measured	Not Measured
Color (Apparent) APHA Units	20	-	270	275
Turbidity, FTU	10	27	30	0
Conductivity, mg/l NaCl	2000	-	1800	67,000
micromhos/cm	3800	-	3400	118,000
Suspended Solids, mg/l	5	-	160	206
Dissolved Solids, mg/l	2850	-	2560	76,000
pH	7.80	-	7.75	10.8
Acidity:				
Total, mg/l CaCO <sub>3</sub>	0	-	0	0
Free, mg/l CaCO <sub>3</sub>	0	-	0	0
Alkalinity (Total)				
P, mg/l CaCO <sub>3</sub>	0	-	0	460
T, mg/l CaCO <sub>3</sub>	195	171	305	610
Hardness:				
Total, mg/l CaCO <sub>3</sub>	1300	1428	1000	45,000
Calcium, mg/l CaCO <sub>3</sub>	1250	571	950	45,000
Halogens:				
Chlorine, mg/l	0.1	-	1.9	0
Chloride, mg/l	1525	-	1275	-
Fluoride, mg/l	0.45	-	0.50	1.36
Sulfate, mg/l	170	-	130	640
Phosphates				
Total, mg/l	1.1	-	1.0	0.7
Nitrogen				
Total, mg/l N	0.55	-	0.43	1.7
Heavy Metals: Iron				
mg/l Fe	0.07	-	0	0.48
Chromate, mg/l Cr+6	0.01	-	0	0
Oxygen (Dissolved), mg/l O <sub>2</sub>	4.7	-	13	4

\*Furnishes cooling water to whole plant

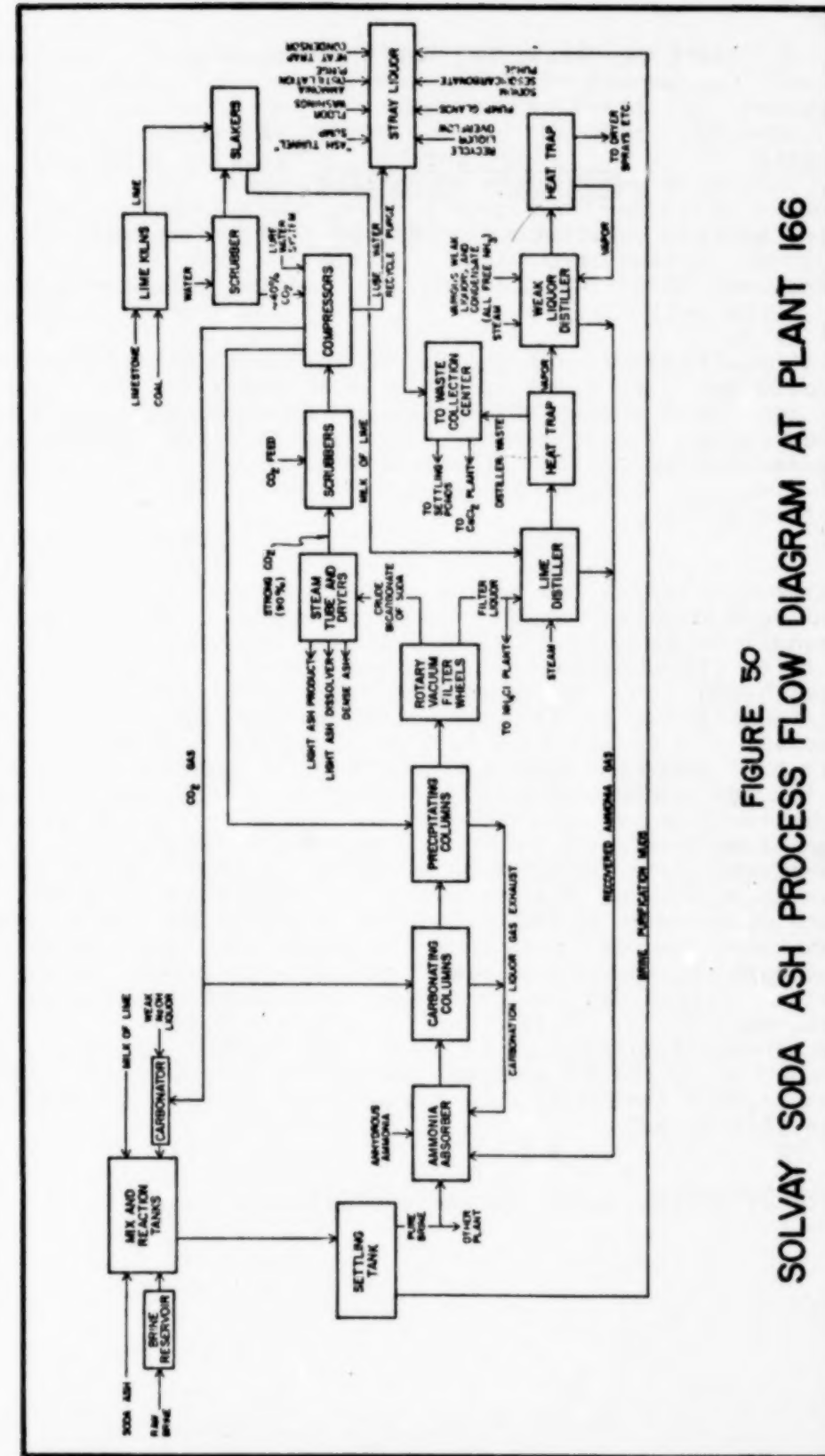


FIGURE 50  
SOLVAY SODA ASH PROCESS FLOW DIAGRAM AT PLANT 166

Waste Products	Process Source	kg/kkg of Soda Ash (lb/ton)
1. $\text{CaCO}_3$	DS, B, P	84.5 (169)
2. $\text{Na}_2\text{CO}_3$	B	0.3 (0.6)
3. $\text{CaSO}_3$	DS	31 (62)
4. $\text{NaCl}$	DS, B	510.5 (1021)
5. $\text{CaCl}_2$	DS	1090 (2180)
6. $\text{Na}_2\text{SO}_4$	B	0.8 (1.6)
7. $\text{Fe}(\text{OH})_3$	B	0.1 (0.2)
8. $\text{Mg}(\text{OH})_2$	DS, B, P	48.5 (97)
9. $\text{CaO}$ (inactive)	DS, B	109.5 (219)
10. $\text{NaOH}$	B	0.05 (0.1)
11. $\text{SiO}_2$	DS, B	58.5 (117)
12. $\text{CaO}$ (active)	DS	24 (48)
13. $\text{NH}_3$	DS	0.15 (0.3)
14. $\text{H}_2\text{S}$	DS	0.02 (0.04)
15. Ash & Cinders	P	40 (80)

DS = Distillation, B = Brine, P = Power

#### Water Inputs to Plant:

Type	l/kkg (gal/ton)	Comments
River	3,650 (875)	Sent to Power Section for boiler feed water
Lake	4,680 (1,120)	Treated prior to use with chlorine
Municipal	2,030 (486)	Majority is sent to Power Section for boiler feedwater

#### Water Flows:

Type	l/kkg (gal/ton)	Recycled
Cooling	52,100 (12,500)	
Process	4.5 (1.1)	0
Sanitary	Est. 74-149 (18-36)	0
Boiler Feed	5,420 (1,300)	0

The maximum process water use is about 149 l/kkg (36 gal/ton), but the average is only 4.5 l/kkg (1.1 gal/ton).

Most of the water use is for cooling purposes and little stream recycling is employed. Treatment methods in use are:



<u>Stream</u>	<u>Source</u>	<u>Treatment</u>	<u>Disposal</u>
Cooling water effluent	Various heat exchangers throughout plant	a. Internal recycle b. Segregation of waste c. Collection and containment of wastes	Disposal to cooling water sewer system
Settling pond effluent	Distiller wastes	Settling out suspended solids with coagulation and precipitation of metals and other chemicals	Discharge to source of cooling water

Individual effluents from this plant are combined with other effluents.

Treatment consists of use of settling ponds and some pH control prior to discharge. The performance of this treatment is detailed below:

<u>Method</u>	<u>Qualitative Rating</u>	<u>Waste Reduction Accomplished</u>
Evaporation of distiller waste	Good	Reduces CaCl by 21 percent NaCl by 4 percent
Settling Ponds	Excellent	Suspended solids reduced by 99 percent+

In addition, two other methods of treatment are used or planned:

- (1) part of the wastes may be used for municipal waste treatment.
- (2) part of the raw distiller waste stream is diverted to a small plant for calcium chloride recovery. About 21 percent of the calcium chloride in the raw waste is recovered on this sidestream.

The plant effluent after treatment contains about 100,000 mg/l dissolved solids (mostly NaCl and CaCl<sub>2</sub>) in the process waste stream and is also fairly high in suspended solids. This type of effluent is typical of a Solvay process plant.

#### Calcium Chloride Recovery

The flow diagram for the calcium chloride recovery process at plant 166 is shown in Figure 51. The waste stream is first cycled through a number of partial evaporation and filtration steps to concentrate the waste solutions. After this, further partial evaporation is used to selectively remove the sodium chloride from solution and then total evaporation is used to recover calcium chloride from the remaining solution.

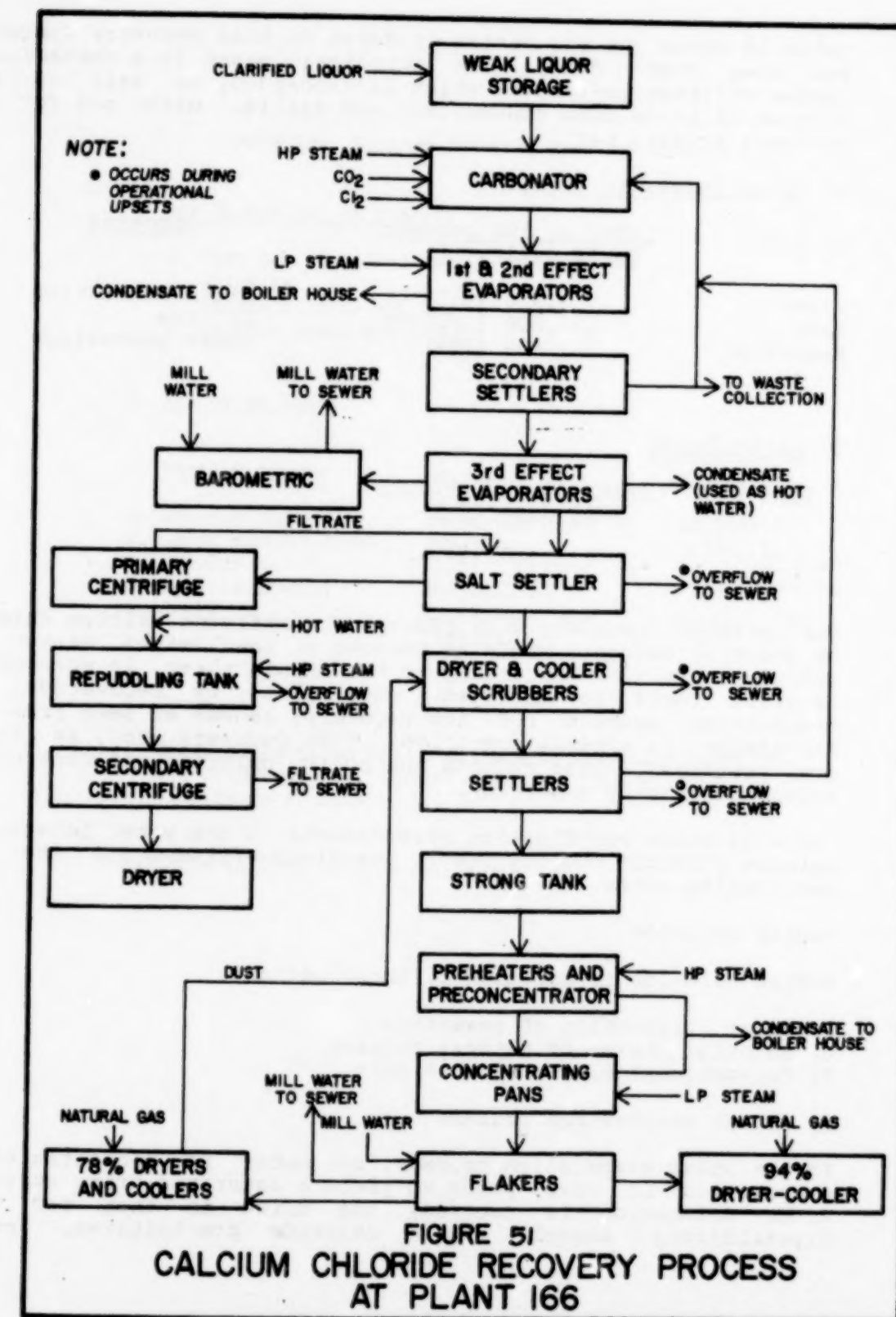


Table 19 shows the raw wastes produced in this recovery operation and some other data. The principal waste is a contaminated sodium chloride co-product which is discarded, as well as some calcium chloride from condensates and spills. Water use for this recovery process is:

#### A. Water Inputs to Plant

Type	1/kgg of 100 percent CaCl <sub>2</sub> (gal/ton)	Comments
River	3,910 (938)	Steam generation
Lake	118,500 (28,400)	Cooling
Municipal	434 (104)	Steam generation

#### B. Water Usage

Type	1/kgg of 100 percent CaCl <sub>2</sub> (gal/ton)
Cooling	118,500 (28,400)
Process	3,850 (923)

The present recovery unit reduces the effluent calcium chloride by about 21 percent. This is because of the limited market for calcium chloride. According to the manufacturer, if more of the material could be marketed, more would be recovered. An evaporation process for its recovery, as can be seen from this discussion, is already operative. This recovery step, as it is now practiced, also reduces the sodium chloride effluent of the Solvay process by 4 percent.

Table 20 shows verification measurements on the water intake, the calcium chloride cooling water, the final effluent and the soda ash cooling water.

Sodium chloride

Sodium chloride is produced by three methods:

- 1) Solar evaporation of seawater;
- 2) Solution mining of natural brines;
- 3) Conventional mining of rock salt.

#### a) Solar evaporation process

In the solar evaporation process, sea water is concentrated by evaporation in open ponds to yield a saturated brine solution. After saturation is reached, the brine is then fed to a crystallizer, wherein sodium chloride precipitates, leaving

TABLE 19. Calcium Chloride Recovery Process

#### A. Raw Materials for Product

1. Soda ash distiller waste
2. Chlorine
3. Carbon dioxide 40% CO<sub>2</sub>
4. Captive steam and power

#### B. Raw Waste Loads

Waste Products	Process Source	kg/kgg (lb/ton) of Product*
1. Ash and cinders	Steam and power	42.5(85)
2. Water purification sludge	Steam	0.75(1.5)
3. NaCl co-product	Evaporation	235(470)
4. CaCl <sub>2</sub>	Condensates and spills	35-50(70-100)

#### C. Comments

Ratio of CaCl<sub>2</sub> to NaCl available in distiller waste is approximately 1.4. Market demand at this location is at a ratio of 10.6 to 1.

\*Product is 100% calcium chloride.

TABLE 20. Verification Measurements at Plant 166

Parameter*	Water Intake	CaCl <sub>2</sub> Cooling Water	Final Effluent	Soda Ash Cooling Water
Flow, cu m/day	Not Measured	Not Measured	17,400	Not Measured
Temperature, °C	11.2	23.8	-	"
Color (Apparent) APHA Units	20	35	275	110
Turbidity, FTU	10	15	0	5
Conductivity, micromhos/cm	2000 (NaCl); 3800	4000 7500	67,000 118,000	21,000 4,400
Suspended Solids	5	10	170	30
pH	7.80	7.95	10.8	7.8
Acidity: Total	0 CaCO <sub>3</sub>	0	0	0
Free	0 "	0	0	0
Alkalinity (Total) P	0 "	0	460	0
T	195 "	190	610	240
Hardness: Total	1300"	1400	45,000	1,270
Calcium	1250"	1350	45,000	1,120
Halogens: Chlorine	0.1	0.6	0	1.7
Chloride	1525	2600	50,000	1,350
Fluoride	0.45	0.55	1.36	0.6
Sulfate	170	170	640	190
Phosphates (Total)	1.1	1.2	0.7	1.6
Nitrogen (Total)	0.55	0.58	1.7	0.48
Heavy Metals: Iron	0.07	0.18	0.48	0.12
Chromate	0.01	0	0	0
Oxygen (Dissolved)	4.7	7.7	4	10
COD	175	-	-	-

\*mg/l unless otherwise specified.

behind a concentrated brine solution (bittern) consisting of sodium, potassium and magnesium salts. The precipitated sodium chloride is recovered for sale and the brine is then further evaporated to recover additional sodium chloride values and is then either stored, discharged back to salt water or further worked to recover potassium and magnesium salts.

In the solar evaporation process, all of the wastes are present in the bittern solution. Typical bittern analysis for the exemplary 059 facility is given in Table 21. No bittern is discharged from this facility. The bittern is stored and, in the past, has been worked for recovery of other materials.

At plant 059, treatment consists of storage and further use of the bittern materials. The plant water usage is:

Type	Use	Source	cu m/day (mgd)	l/kg (gal/ton)	Recycle
Process	Refining process	Well	2,270 (0.60)	894 (214)	100 percent
Process	Raw Material	Bay	327,000 (86.4)	129,000 (30,900)	None

As the biterrens are stored and further worked, there is no discharge. Eventual total evaporation after further bittern use yields only solid wastes. Sufficient land and ponding area is available at the 059 facility to store biterrens for the next 30-50 years.

#### b) Solution brine-mining process

Saturated brine for the production of evaporated salt is usually obtained by pumping water into an underground salt deposit and removing the saturated salt solution from an adjacent interconnected well, or from the same well by means of an annular pipe. Besides sodium chloride, the brine will contain some calcium sulfate, calcium chloride, magnesium chloride, and lesser amounts of other materials including iron salts and sulfides.

The chemical treatment given to brines varies from plant to plant depending on the impurities present. Typically, the brine is first aerated to remove hydrogen sulfide and, in many cases, small amounts of chlorine are added to complete sulfide removal and oxidize all iron salts present to the ferric state. The brine is then pumped to settling tanks where it is treated with soda ash and caustic soda to remove most of the calcium, magnesium and iron present as insoluble salts. After clarification to remove these insolubles, the brine is sent to multiple-effect evaporators. As water is removed, salt crystals form and are removed as a slurry. After screening to remove lumps, the slurry is washed with fresh brine to remove fine



TABLE 21. Chemical Analysis of Bittern

Parameter*	
pH	7.8
Total Solids	241550
Total Volative Solids	86600
Total Suspended Solids	1760
Total Dissolved Solids	239790
Alkalinity as CaCO <sub>3</sub>	2800
BOD	198
COD	6350
Ammonia as N	0.702
Kjeldahl Nitrogen Total	32.610
Nitrate as N	37.50
Phosphorus Total as P	0.22
Chloride	158000
Cyanide	0.04
Fluoride	74.90
Phenols	0.064
Sulfate as S	21000
Sulfide as S	2
TOC	900
Aluminum	2.5
Arsenic	0.04
Cadmium	0.02
Calcium	450
Chromium	0.02
Iron	6.5
Mercury	0.001
Sodium	5500
Titanium	0.02
Zinc	0.19

\* All units mg/l unless otherwise specified.

crystals of calcium sulfate from the mother liquor to the slurry. These solids are returned to the evaporator. The calcium sulfate concentration in the evaporator eventually builds up to the point where it must be removed by "boiling out" the evaporators.

The washed slurry is filtered, the mother liquor is returned to the evaporators, and the salt crystals from the filter are dried and screened. Salt thus produced from a typical brine will be of 99.8 percent purity or greater. Some plants do not treat the raw brine, but control the calcium and magnesium impurities by watching the concentrations in the evaporators and bleeding off sufficient brine to maintain predetermined levels. By such methods, salt of better than 99.5 percent purity can be made. In either case, the final screening of the dried salt yields various grades depending on particle size. The facility at plant 030 is similar to the standard flow diagram shown in Section IV.

A detailed list of the raw wastes and their process sources is shown below. These include wastes from the multiple evaporators and dryers, sludges from basic purification, as well as water treatment chemicals used for the cooling water:

Waste Products	Process Source	Avg. kg/kkg of Product (lb/ton)
NaOH	Boiler Blowdown	0.0055 (0.011)
Na <sub>3</sub> PO <sub>4</sub>	" "	0.0015 (0.003)
Na <sub>2</sub> SiO <sub>3</sub>	" "	0.0025 (0.005)
Na <sub>2</sub> SO <sub>3</sub>	" "	0.0015 (0.003)
NaCl & CaSO <sub>4</sub>	Purge from multiple evaporator	0.045 (0.090)
NaCl	Evaporator	0.04 (0.08)
NaCl	Barometric condenser	1.1 (2.2)
NaCl	Miscellaneous sources	-
Brine sludges	Brine purification	91 kkg/year (100 ton/year)

The brine sludges are returned to the brine wells for settling and disposal.

Well water for brine field use is taken into the plant at a rate of 2,240 l/kkg of product (536 gal/ton). Lake water for cooling and other uses is drawn into the plant at a rate of 48,000 l/kkg (11,400 gal/ton).

Use	Flow	Recycle
Cooling (barometric condensers)	41,700 l/kkg (10,000 gal/ton)	none
Other (dust collection pumps)	6,400 l/kkg (1,540 gal/ton)	90 percent

Treatments of the effluent streams are as follows:

<u>Stream No.</u>	<u>Source</u>	<u>Treatment</u>
1	Condenser Discharge	To Lake
2	Storm Drain	To Lake
3	Tunnel Line (Lake Water)	To Lake
4	Ash Lime Discharge	Recycled

The storm drain flow cited above was 3,790 l/kg of product (910 gal/ton) on the average.

The plant effluent streams #1 and #2 after treatment consist solely of streams containing 100 mg/l chloride at a pH of 8.2. Chloride concentration at the plant intake was given as 70-80 mg/l, with a pH of 8.2. Table 22 shows verification measurements on the plant intake and condenser discharge (stream #1) effluent. The chloride content and pH as stated are verified within a reasonable margin.

#### Sodium Dichromate and Sodium Sulfate

Sodium dichromate is prepared by calcining a mixture of chrome ore ( $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ ), soda ash and lime, followed by water leaching and acidification of the soluble chromates. The insoluble residue from the leaching operation is recycled to leach out additional material.

During the first acidification step, the pH of the chromate solution is adjusted to precipitate calcium salts. Further acidification converts it to the dichromate and a subsequent evaporation step crystallizes sodium sulfate (salt cake) out of the liquor. The sulfate is then dried and sold. The solutions remaining after sulfate removal are further evaporated to recover sodium dichromate. Chromic acid is produced from sodium dichromate by reaction with sulfuric acid. Sodium bisulfate is a by-product. Figure 52 shows a detailed flowsheet for the exemplary facility at plant 184.

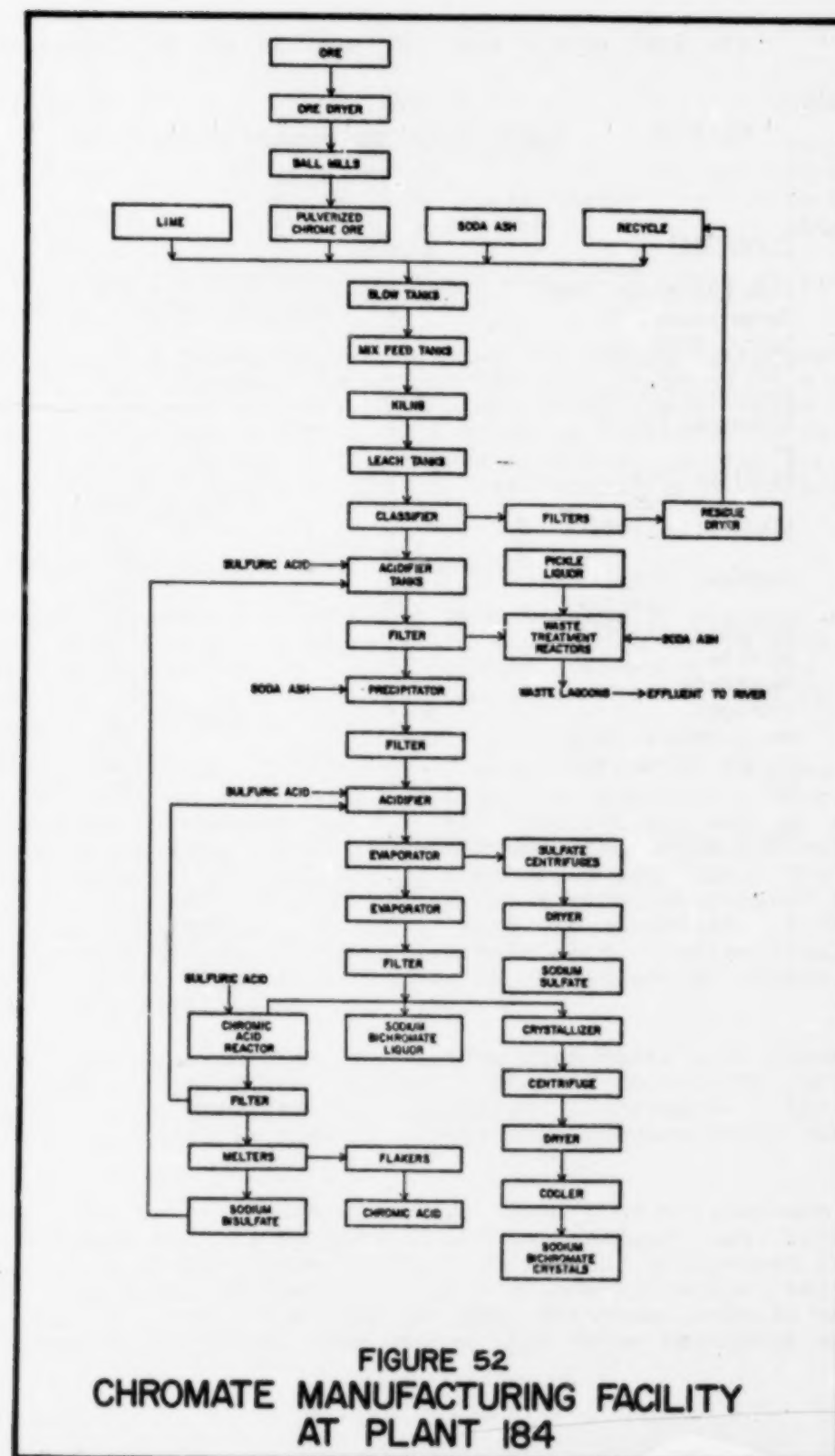
Plant 184 manufactures only sodium dichromate and chromic acid. However, some other chromate plants do convert part of their chromic acid products to potassium dichromate. All of this latter material is made in plants that produce other chromates.

The raw waste loads expected from the manufacture of sodium dichromate and its by-product sodium sulfate are given below. The bulk of the waste originates from the undigested portions of the ores used. These materials are mostly solid wastes. The wastes arising from spills and washdowns contain most of the hexavalent chromium. The wastes from water treatment and boiler

TABLE 22. Verification Measurements at Plant 030

<u>Parameter*</u>	<u>Intake</u>	<u>Condenser Discharge</u>
Flow, cu m/day (MGD)	37,900(10)	37,900(10.0)
Temperature, °C	13	22.5-23.0
Color, APHA Std.	40	40
Turbidity(FTU)	10	15
Conductivity(NaCl)	225	320
Suspended Solids	0	0
pH	8.0	8.1
Acidity: Total	0	0
Free	0	0
Alkalinity (Total) P	0	0
T	139	140
Hardness: Total	171	189
Calcium	128	147
Halogens: Chloride	65	120
Sulfate	13	37
Phosphates	0.07	0.1
Nitrogen	0.17	0.17
Heavy Metals: Iron	0.24	0.23
Oxygen (Dissolved)	-	2.8
COD	55	50

\*mg/l unless otherwise specified.



blowdowns are principally dissolved sulfates and chlorides. The manufacture of chromic acid contributes no additional wastes.

Waste Product	Process Source	kg/kg of Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> Product (lb/ton)	
		Average	Range
1. Chromate wastes (Materials not digested in H <sub>2</sub> SO <sub>4</sub> )	Residues	900 (1800)	-
2. Washdowns* spills, etc.	--	0.75 (1.5)	0.5-1 (1-2)
3. Blowdown	Boilers and cooling towers	--	0.5-1 (1-2)

\*Includes contributions from the chromic acid unit.

Water intake to this facility consists of river water and well water in the following amounts based on sodium dichromate product: 12,700 l/kg (3,030 gal/ton) and 1,840 l/kg (440 gal/ton) respectively. The boiler feed comes from the river water feed and is softened prior to use. The well water is all filtered, softened and chlorinated.

#### Water Use:

Type	l/kg of sodium dichromate (gal/ton)	Percent Recycled
Cooling	275,000 (66,000)	98.2
Products and Evaporation	5,400 (1,300)	0
Waste Treatment	8,860 (2,120)	0
Sanitary	255 (60)	0

Waste waters are treated with pickle liquor to effect reduction of chromates present. All effluent waters are lagooned to settle out suspended solids. This treatment removes 99 percent of the hexavalent chromium and the discharge contains 0.01 mg/l. The lagoon discharges to a nearby river when full.

All rainwater, washdowns, spills and minor leaks in the part of the plant which handles hexavalent chromium are captured in the area's sumps and used in the process. Storage facilities are provided to contain a heavy rain and return the water either to the process or to treatment. Separate rainwater drainage is provided for areas not handling hexavalent chromium. Sewers are continuously monitored. A batch system is used in the treatment process. Each batch is treated and analyzed before release to the lagoon.



Data on the effluent from this exemplary chromate treatment facility are presented below:

	Average	Range
Flow, liters/kg (gal/ton)	8,860 (2,120)	-
Total Suspended Solids, mg/l	14	1-24
Total Dissolved Solids, mg/l	10,000	5,000 - 13,000 (mostly chlorides)
pH	7.2	6.0 - 8.5
Cr+3, mg/l	0.14	0.01 - 0.31
	(mostly in form of suspended solids)	
Cr+6, mg/l	0.01	

The chromium content has been significantly reduced. However, the amount of sodium chloride being discharged is significant. Based on the porous nature of the present lagoon walls and the high dissolved solids content discharged into the river, this plant is considered exemplary only from the standpoint of chromate control and treatment.

Table 23 gives a more detailed presentation for the river intake and plant effluent from this facility. The composition of river water taken near the plant and the plant effluent determined on two separate occasions are shown as a range of values. These data were furnished by the plant.

Tables 24 and 25 present data obtained by sampling for this facility. Table 24 shows an analysis of river water drawn adjacent to the plant. Table 25 shows the compositions of waste stream before and after passage through the pickle liquor treatment unit.

#### Sodium Metal

Sodium is manufactured by electrolysis of molten sodium chloride in a Downs electrolytic cell. After salt purification to remove calcium and magnesium salts and sulfates, the sodium chloride is dried and fed to the cell, where calcium chloride is added to give a low-melting  $\text{CaCl}_2\text{-NaCl}$  eutectic, which is then electrolyzed. Sodium is formed at one electrode, collected as a liquid, filtered and sold. The chlorine liberated at the other electrode is first dried with sulfuric acid and then purified, compressed, liquified and sold. Figure 53 shows the process in use and waste treatment facilities at plant 096.

There is no waste during operation of an individual cell for the molten salt electrolysis step in the Downs cell process. The cells are run in banks, and individual cells are cleaned out and refilled after the electrolyte is depleted. All of the wastes arise from this cleaning and refilling of individual cells.

TABLE 23. Intake and Effluent Composition at Plant 184

Parameter	River Water	Plant Effluent
Total Solids	79	330-334
Organic Solids	45	93-104
Mineral Solids	34	230-232
Alkalinity as $\text{CaCO}_3$ (methyl-orange)	2.0	0.0
Alkalinity (phenolphthalein)	0.0	0.0
Free Carbon Dioxide	1.6	1.0-17.0
Total Hardness (as $\text{CaCO}_3$ )	15	209.3-238.7
Total Hardness (grains per gallon)	0.88	12.2-12.8
pH	6.4	7.4-8.4
Analysis of Mineral Solids:		
Silica ( $\text{SiO}_2$ )	2.6	5.0-6.0
Iron Oxide ( $\text{Fe}_2\text{O}_3$ )	0.4	0.1-0.3
Alumina ( $\text{Al}_2\text{O}_3$ )	0.8	0.0
Lime ( $\text{CaO}$ )	5.6	114.4-115.5
Magnesia ( $\text{MgO}$ )	2.0	0.8-5.0
Sulphate ( $\text{SO}_3$ )	6.8	3.4
Chloride ( $\text{Cl}$ )	8.9	1.3-1.8
Soda ( $\text{Na}_2\text{O}$ )	5.7	8.2-10.4
Manganese (Mn)	0.0	0.0
Fluoride (F)	0.0	0.0
Biochemical Oxygen Demand ( $\text{BOD}_5$ )	less than 5	-
Color (Pt-Co)	130	
Chromium (Cr)	-	**
Tannin	2.6	**

\*mg/l unless otherwise specified

\*\*None found

TABLE 24. Analysis of River Water at Plant 184

<u>Parameter</u>	<u>Measurements (mg/l unless otherwise specified)</u>
Color, APHA Units	270
Turbidity, FTU	5
Conductivity	35 NaCl eq.
Suspended Solids	5
pH	6.59
Alkalinity (Total)	phen-0/Total-20 (as CaCO <sub>3</sub> )
Hardness: (Total)	23 (as CaCO <sub>3</sub> )
(Calcium)	15
Halogens: Chloride	11
Sulfate	0
Phosphate	0.38
Nitrate	0.13 (as N)
Heavy Metals: Iron	1.5
Chromium (Cr+6)	0*

\*less than 20 mcg/l

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TABLE 25. Analysis of Waste Treatment Streams at Plant 184

<u>Parameter</u>	<u>Before Treatment</u>	<u>After Treatment</u>
Flow	Batch volume - 28,700 liters	Batch volume - 30,400 liters
Temperature, °C	49	61
Color	500 (supernatant liquid)	70
Conductivity	5000 NaCl	14,500
Dissolved Solids	10,700	18,000
Suspended Solids	170,000	154,000
pH	10 (straight); 9.3 (dilution)	9.1 (supernatant, fresh); 8.4 (filtered, 30 days old)
Alkalinity (Total)	phen-0/total-1000 (as CaCO <sub>3</sub> )	phen-2/total-23 (as CaCO <sub>3</sub> )
Hardness: Total	600 (as CaCO <sub>3</sub> )	6,000
Calcium	520 (as CaCO <sub>3</sub> )	6,000
Halogens: Chloride	310	8,700
Sulfate	3,900	1,900
Phosphate	0.7	0.7
Nitrate	9.8 (as N)	-
Heavy Metals:		
Chromium (Cr+6)	1,300	0.01
Iron	-	0.60
Oxygen (Dissolved)	10.4	-

\*mg/l unless otherwise specified.

5732

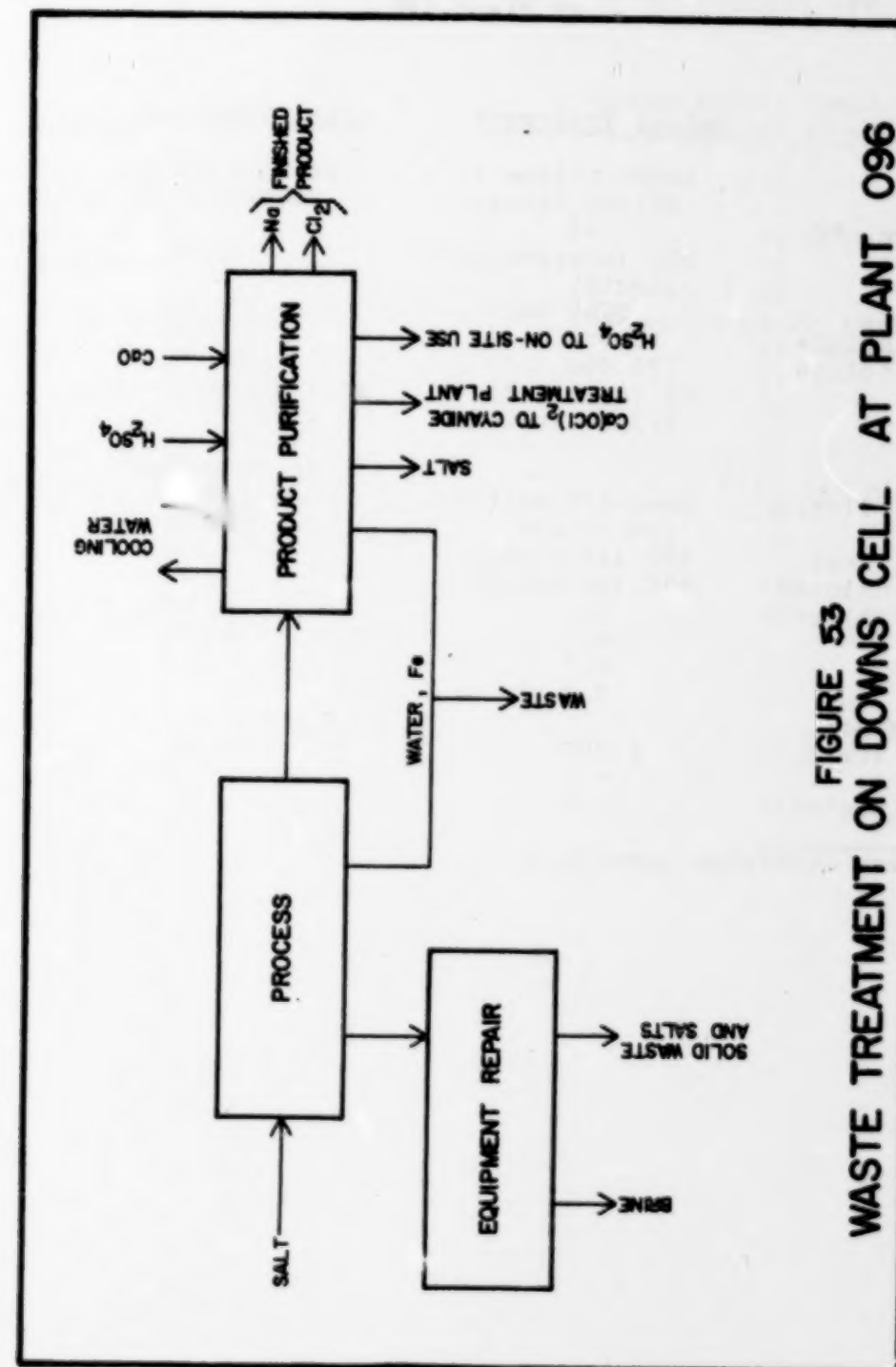


FIGURE 53  
WASTE TREATMENT ON DOWNS CELL AT PLANT 096

The wastes produced by sodium manufacture at plant 096 are shown below. Several of the expected wastes are not present. This is due to the reuse of materials in other parts of the facility to make other products. For example, the sulfuric acid used in drying the chlorine is reused.

Waste Products	Process Source	kg/kg of Product (lb/ton)
NaCl	Process	50-65 (100-130)
Misc. Alkaline Salts	Process	25-35 (50-70)
Ca (OCl) <sub>2</sub>	Chlorine Recovery	45-75 (90-150)
Fe	Cooling Tower	0.065-0.095 (0.13-0.19)

The process does not normally shut down. The discharges result from the replacement of cells.

Cooling tower blowdowns and residual chlorine from tail gas scrubbers are discharged without treatment. The stream containing calcium hypochlorite wastes is used to treat cyanide wastes. Cooling water is discharged without treatment and tank wash and runoff water are first ponded to settle out suspended materials and then discharged.

The water input to the plant is well water in the amount of 2,730 cu m/day or 46,300 l/kg of product (11,100 gal/ton), having an impurity content of:

Total Solids	110-125 mg/l
CO <sub>2</sub>	30-60 mg/l
Hardness (as Ca)	80-100 mg/l
Fe	1-3 mg/l
Cu	0.02-0.06 mg/l
Zn	0.02 mg/l
Sulfate	2-7 mg/l
Alkalinity (CaCO <sub>3</sub> )	70-100 mg/l

The water use within the plant is as follows:

Use	Flow	Amount
Cooling	29,100 cu m/day (7.7 mgd)	497,000 l/kg (119,000 gal/ton)
Process	530 cu m/day (0.14 mgd)	9,000 l/kg (2,150 gal/ton)

Table 26 lists the various plant waste streams and their compositions.

These stream effluents consist mostly of dissolved sodium chloride and other chlorides. Table 27 shows the results of analyses of simultaneous samples from three of the waste streams (those



TABLE 26. Plant 096 Effluent

Parameter*	Stream No. 1**	Stream No. 2***	Stream No. 3****	Stream No. 4*****
Flow, cu m/day (MGD)	409(0.108)	133(0.035)	1,780(0.470)	409(0.108)
TSS	30-50	50-70	5-10	-
TDS	400-600	-	300-400	-
BOD	-	-	-	-
COD	-	-	-	-
pH	6.5-7.5	10.5-12.0	6.7-7.5	-
Fe	2	1-2	2-3	-
Chloride	100-150	10,000-30,000	50-100	13,000
Chlorine	-	4,000-6,000	20-100	-
Sulfate	-	-	25-50	-
Total Hardness	-	-	180-225	-
Phosphate	0.2	-	-	-
Turbidity(FTU)	25-30	40-60	125	-
Color(APHA)	15	15	15	-
Acidity(Free)	20-30	20-30	-	-
Alkalinity (Total)	-	4,000-6,000	-	-
Hardness(Ca)	-	25,000-30,000	-	-

\*All units mg/l unless otherwise specified.

\*\*Cooling Tower Blowdown, Cl<sub>2</sub> Residual.

\*\*\*Calcium hypochlorite used to treat cyanide wastes in another process.

\*\*\*\*Cooling water.

\*\*\*\*\*Runoff, excess calcium hypochlorite, tank washup.

Note: There is also 2,270 liters/day (600 GPD) used sulfuric acid sent for use elsewhere in the complex and not discharged into surface streams.

TABLE 27. Plant 096 Effluent

Parameter*	Stream No. 2	Stream No. 3	Stream No. 4
Flow, cu m/day (MGD)	-	-	-
Plant	-	-	-
VM**	133(0.035)	1,590(0.42)	-
Temperature, °C	-	-	-
Plant	-	-	-
VM	21.5	22	20
Color(True), APHA Units	-	-	-
Plant	15	15	15
VM	300	30	260
Turbidity, Jackson Units	-	-	-
Plant	26	25	58
VM	82	10	45
Suspended Solids	-	-	-
Plant	39	6	137
VM	39	11	90
Dissolved Solids	-	-	-
Plant	574	355	-
VM	479	266	35,800
pH	-	-	-
Plant	6.5	6.45	11.9
VM	6.55	6.44	11.9
Acidity(Free)	-	-	-
Plant	19.5	37.5	-
VM	-	-	-
Alkalinity(CaCO <sub>3</sub> )	-	-	-
Plant	-	-	-
VM	48	57	4,500
Chlorine	-	-	-
Plant	0	0.6	64,000
VM	0	0.2	2,400
Chloride	-	-	-
Plant	121	92	17,800
VM	125	90	26,500
Sulfate	-	-	-
Plant	-	26	-
VM	-	10	-
Fe	-	-	-
Plant	0.33	0.69	0.92
VM	0.22	2.7	0.7

\*mg/l unless otherwise specified.

\*\*Verification measurement

corresponding to streams 2, 3, and 4 of Table 26). Good agreement between the results was generally obtained.

This facility has good pH and suspended solids control and reuse of some wastes, but there are large amounts of chlorides being discharged which may be recycled for process reuse.

#### Sodium Silicate

Sodium silicate is manufactured by the reaction of soda ash or anhydrous sodium hydroxide with silica in a furnace, followed by dissolution of the product in water under pressure to prepare sodium silicate solutions. In some plants, the liquid silicate solutions are then further reacted with sodium hydroxide to manufacture metasilicates which are then isolated by evaporation and sold. Figure 54 shows the total system diagram for plant 072.

The raw waste loads for plant 072 are listed below. These wastes consist mostly of sodium silicate and unreacted silica:

Waste Products	Process Source	Avg. kg/kg of Dry Basis Product (lb/ton)
Sodium Silicate	Scrubbers	37 (74)
Silica	Scrubbers	2.85 (5.7)
NaOH/Silicates	Washdowns	0.39 (0.78)

Data on in-plant water use could not be obtained from plant 072. However, the water use data from another plant (134) is given below on the basis of unit weight of product (dry basis). The water intake is 2,900 l/kg (710 gal/ton) which is used as follows:

Water Use	l/kg (gal/ton)
Process water	1,020 (245)
Boiler blow-down, Compressor cooling, Wash-down, Tank cleaning, and misc.	610 (147)
Steam, Evaporation, and other losses	1,330 (319)

At plant 072 all scrubber and washdown waters are sent to a totally enclosed evaporation pond. There is no plant effluent.

#### Sodium Sulfite

Sodium sulfite is manufactured by reaction of sulfur dioxide with soda ash. The crude sulfite formed in this reaction is then purified, filtered to remove insolubles from the purification

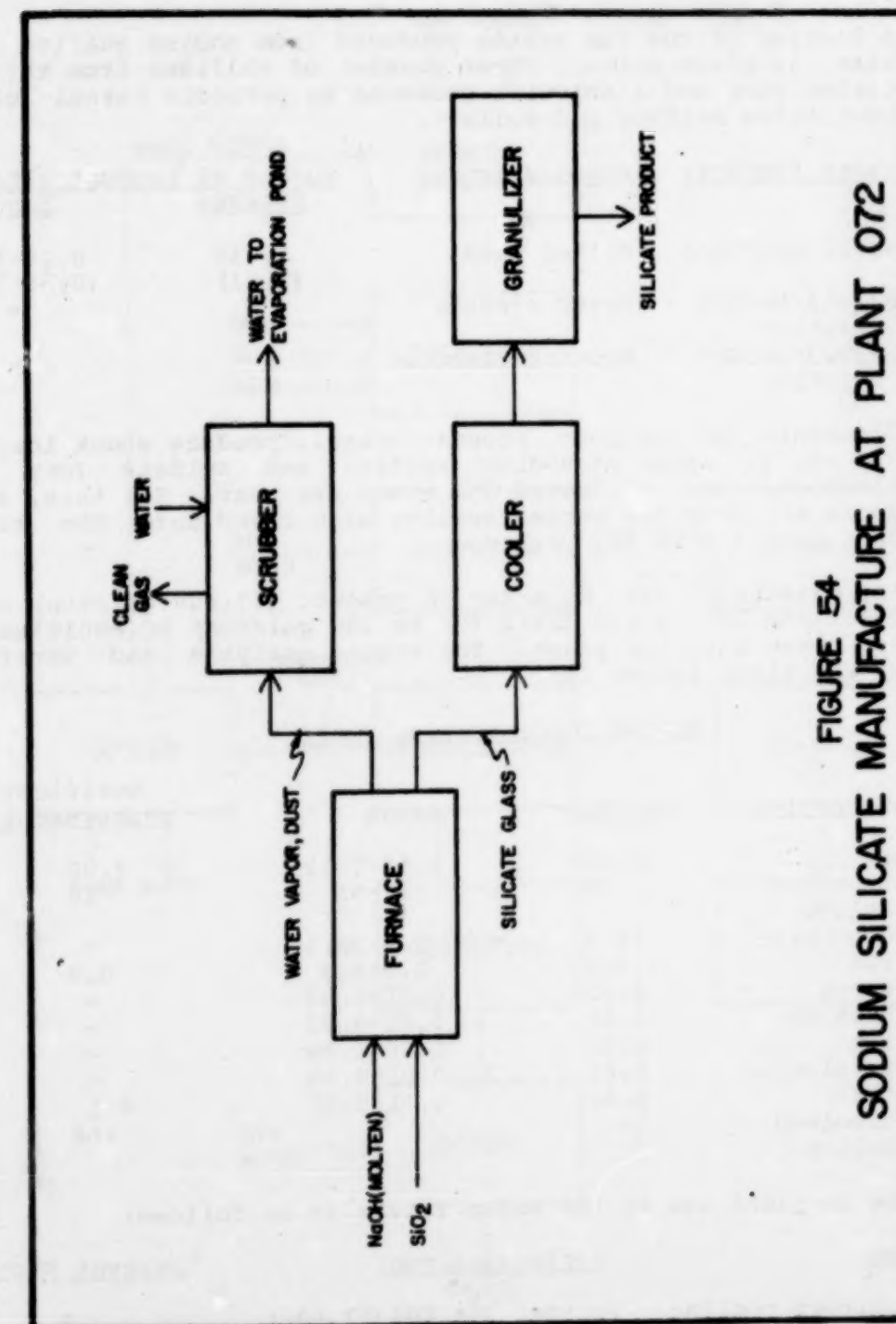


FIGURE 54  
SODIUM SILICATE MANUFACTURE AT PLANT 072

step, crystallized, dried and shipped. A process diagram for plant 168 is given in Figure 55.

A listing of the raw wastes produced from sodium sulfite production is given below. These consist of sulfides from the purification step and a solution produced by periodic vessel cleanouts containing sulfite and sulfate.

Waste Products	Process Source	kg/kkg of Product (lb/ton)	
		Average	Range
Metal sulfides	Filter wash	0.755 (1.51)	0.19-1.44 (0.38-2.88)
Na <sub>2</sub> SO <sub>3</sub> /Na <sub>2</sub> SO <sub>4</sub> solution	Dryer ejector	-	-
Na <sub>2</sub> SO <sub>3</sub> /Na <sub>2</sub> SO <sub>4</sub> solution	Process cleanout	-	-

Cleanouts of various process vessels produce shock loads up to 9.1 kkg (10 tons) of sodium sulfite and sulfate (dry basis). Cleanouts are conducted 3-6 times per year. For this, separate tanks are used for surge capacity with bleed into the treatment unit over a 5-10 day period.

Approximately 244 cu m/kkg of product (57,600 gal/ton) of river water and 290 to 630 l/kkg (70 to 150 gal/ton) of municipal water are taken into the plant. The stated analysis and verification of the river intake is:

Stated Concentration (mg/l)			
Parameter	Average	Range	Verification Measurement (mg/l)
pH	(6.80)	5.68-7.12	7.00
Suspended Solids	28	10-45	10
POC	14.8	1.4-38.5	-
Iron	2.6	1.5-4.9	0.9
Copper	0.02	0.01-0.02	-
Chromium	0.01	0.01-0.02	-
Zinc	0.49	0.08-1.84	-
Nickel	0.01	0.01-0.02	-
Lead	0.02	0.01-0.07	0.1
Dissolved Solids	-	-	168

The in-plant use of the water intake is as follows:

Use	l/kkg (gal/ton)	Percent Recycle
Indirect cooling	Approx. 244,000 (57,600)	0
Process (condensate)	Approx. 170 (40)	0
Dryer, Ejector	290 to 630	0
Filter Wash	(70 to 150)	0

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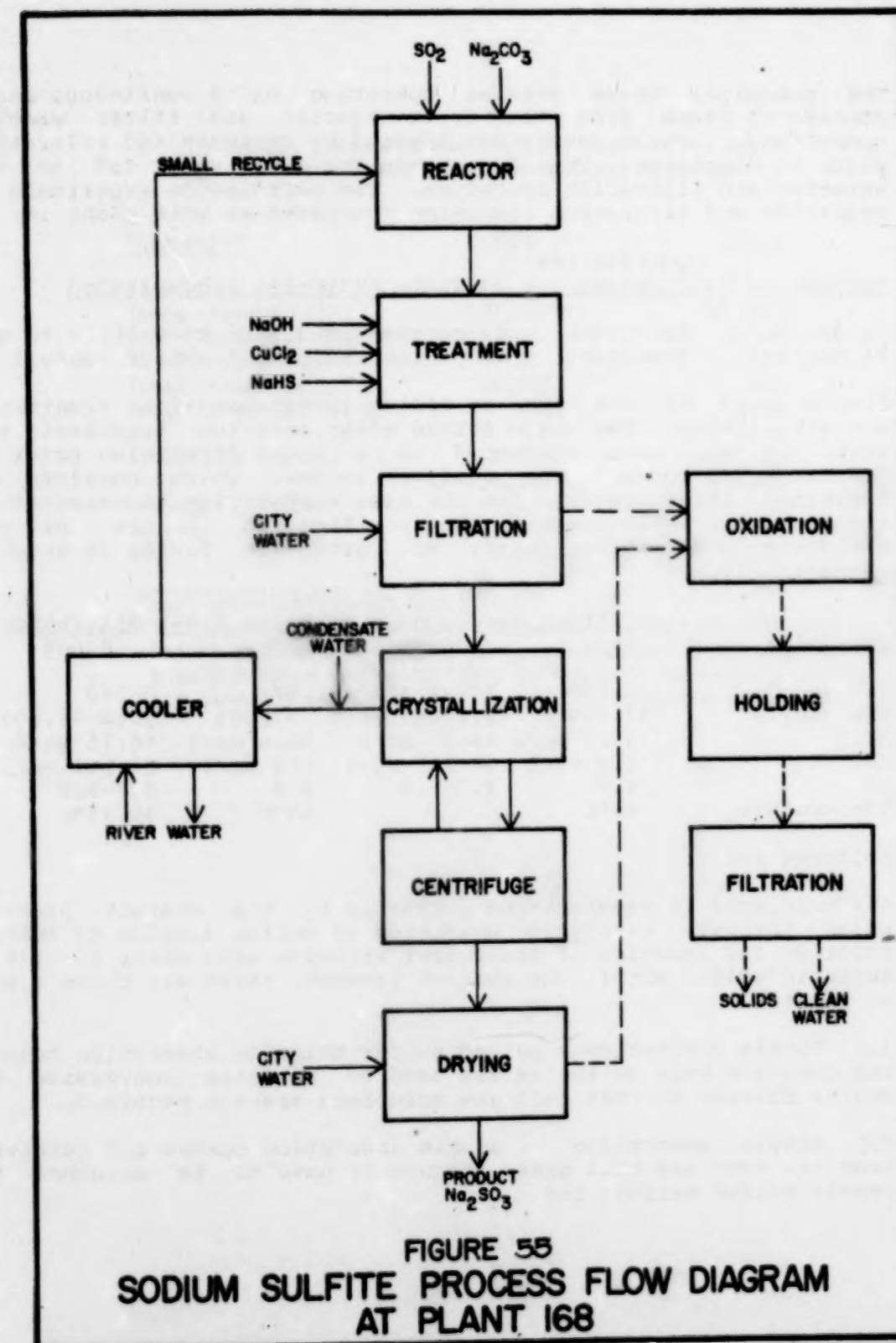


FIGURE 55  
SODIUM SULFITE PROCESS FLOW DIAGRAM  
AT PLANT 168



The principal waste streams operating on a continuous basis consist of flows from the dryer ejector and filter washing operations. These waters are treated by aeration and filtration prior to discharge. Vessel washouts are also subjected to the aeration and filtration procedure. The performance experience of oxidation and filtration treatment processes at this plant is:

Method	Qualitative Rating	Waste Reduction Accomplished
Oxidation	Excellent	94 percent oxidation of sulfite to sulfate
Filtration	Excellent	98 percent suspended solids removal

Compositions of the process effluents streams after treatments are given below. The waste stream after aeration treatment and after it has been subjected to a final filtration prior to discharge are shown. The cooling stream, which consists of untreated river water, has the same composition as measured at the intake. Measurements for verification of the process effluents and cooling water are given in Tables 28 and 29, respectively.

Parameter	After Aeration		After Final Filtration	
	Ave.	Range	Ave.	Range
TSS (mg/l)	2,200	700-4,100	97	3-240
TDS (mg/l)	57,000	46,000-70,000	57,000	46,000-70,000
BCD5	56.8 mg/l	46-71 mg/l	56.8 mg/l	46-71 mg/l
COD	118 mg/l	64-161 mg/l	118 mg/l	64-161 mg/l
pH	9.8	9.7-9.9	9.8	9.7-9.9
Temperature	65°C	-	43°C	38-49°C

#### Sulfuric Acid

Sulfuric acid is manufactured primarily by the contact process which involves catalytic oxidation of sulfur dioxide to sulfur trioxide and reaction of the sulfur trioxide with water to yield sulfuric acid. Within the contact process, there are three types of plants.

(1) Double absorption - paired sulfur trioxide absorption towers and catalyst beds in series are used to maximize conversion of sulfur dioxide so that tail gas scrubbers are not required.

(2) Single absorption - single absorption towers and catalyst beds are used and tail gases frequently have to be scrubbed to remove sulfur oxides; and

TABLE 28. Measurements of Plant 168 Process Waste Streams Before and After Treatment

Parameter*	Before**	After
Flow	(Batch Process)	(Batch Process)
Temperature, °C(°F)	76.7(170)	76.7(170)
Color(Apparent) APHA Std.	500	500
Turbidity, FTU	500	380
Total Dissolved Solids	88,200	93,900
Total Suspended Solids	780	2,010
pH	11.0	11.2
Alkalinity (Total) P	9,000	2,500
T	24,000	4,800
Hydrogen Sulfide	0	0
Sulfite	60,000	170
COD	8,000	250

\*mg/l unless otherwise specified.

\*\*This sample was collected from the full oxidation tank just before the waste treatment process was begun. This was necessary because the waste lines to the tank are not accessible for sampling and the only outlet valve is on the tank itself.

TABLE 29. Plant 168 Cooling Water Measurements

Parameter*	Intake	Effluent
Temperature, °C	17	21
Color(Apparent) APHA Std.	95	65
Turbidity, FTU	25	15
Conductivity, as NaCl	130	120
Suspended Solids	10	8
pH	7.00	7.08
Acidity: Total	0	0
Free	0	0
Alkalinity (Total) P	0	0
T	40	40
Hardness: Total	73	76
Calcium	50	51
Halogens: Chlorine	24	24
Sulfate	53	55
Phosphates	0.72	0.66
Nitrate	0.33	0.32
Heavy Metals: Iron	0.86	0.78
Hydrogen Sulfide	0	0
Sodium Sulfite	3	4

\*mg/l unless otherwise specified.

(3) Spent acid plants - these plants use spent sulfuric acid in place of, or in addition to, sulfur as a raw material. While the acid production parts of these plants are the same as those for single absorption, these plants are unique because of the spent acid pyrolysis units used to convert the waste sulfuric acid raw materials to a sulfur dioxide feed stream.

In this section, only the first two types of plants are considered.

#### Double Absorption

In the double absorption contact process, sulfur is burned to yield sulfur dioxide which is then passed through a catalytic converter with air to produce sulfur trioxide. The sulfur trioxide is then absorbed in 95-97 percent sulfuric acid. The gases emerging from the absorber are fed to a second converter to oxidize the remaining sulfur dioxide to sulfur trioxide which is then absorbed in a second absorption tower. The tail gases are vented to the atmosphere. Figure 56 shows a detailed process flow sheet for plant 086.

At plant 086, only cooling water is discharged. In double absorption plants, the tail gases are sufficiently depleted to sulfur oxides that there is no need for gas scrubbers. Also, at this plant, use of extensive maintenance and leak prevention has been employed to prevent discharge of any product acid.

The table below shows water usage at plant 086. Most water is used for cooling. Process water is consumed to make sulfuric acid and is not discharged. The only plant effluent is the cooling water used in the heat exchangers and associated water treatment chemicals.

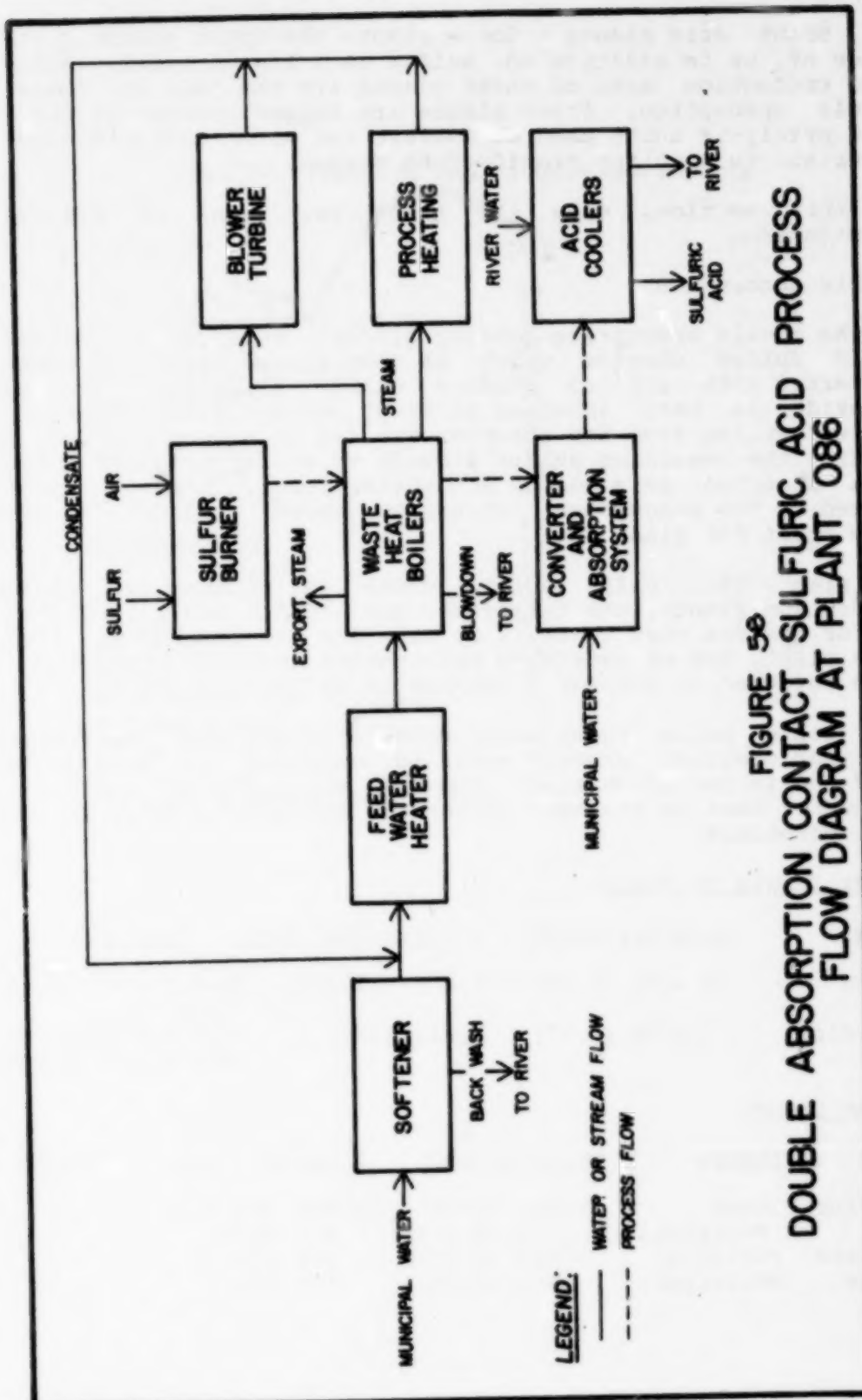
#### Water Inputs to Plant:

Type	cu m/day (mgd)	l/kg (gal/ton)	Comments
River	35,200 (9.30)	55,600 (13,300)	Used for cooling only
Municipal	1,020 (0.27)	1,610 (386)	Used for process steam and cooling

#### Water Usage:

Type	Source	cu m/day (mgd)	l/kg (gal/ton)	Percent Recycled
Cooling	River	35,200 (9.30)	55,600 (13,300)	0
	Municipal	295 (0.078)	463 (111)	0
Process	Municipal	117 (0.031)	184 (44)	0
Steam	Municipal	610 (0.161)	960 (230)	0





The only effluent from this facility is once-through cooling water. Table 30 shows verification measurements for the water intake and effluent.

#### Single Absorption

The single absorption process differs from that previously described only in the arrangement of converters and absorbers. The rest of the process is the same. For the single absorption process, the sulfur dioxide is passed through one or more converters and then into one or more absorbers prior to venting to the atmosphere. This arrangement is less effective for both conversion of sulfur dioxide to sulfur trioxide and for absorption of the sulfur trioxide into the absorber sulfuric acid. As a result, the tail gases may have to be scrubbed, creating a waterborne waste not present for double absorption plants. The exemplary plant is plant 141.

For the single absorption sulfur-burning process, there are no wastes from the sulfuric acid process itself. Wastes arise from the use of water treatment chemicals. The raw wastes are iron, silicon, calcium and magnesium salts from water treatment. This does not cover spent acid plants based on single absorption.

Most of the cooling water used at this plant is recycled and only 5 percent emerges from the plant. This is sent to evaporation ponds, from which there is no discharge. The water input is well water in the quantity of 606 cu m/day (0.160 mgd) or 1,670 l/kg of product (400 gal/ton). This water is used as follows:

Type	cu m/day (mgd)	l/kg (gal/ton)	Recycled
Cooling	560 (0.148)	1,540 (370)	95
Process	45.5 (0.012)	125 (30)	0

All waterborne wastes are sent to an evaporation pond. There is no discharge. Table 31 shows verification measurements on the intake water, the effluent going to the evaporation pond, and the evaporation pond water, respectively.

#### Titanium Dioxide

##### a) Chloride process

Virtually the same process is used at the two chloride process facilities studied (plants 009 and 160). The only process differences lie in the types of ore used. Plant 160 employs a unique process using an ore containing 66 percent titanium dioxide, while plant 009 uses only 95 percent plus grades of rutile and upgraded ilmenite. Figure 57 and 58 show the process flows within the 009 facility.



TABLE 30. Intake and Effluent Measurements at Plant 086

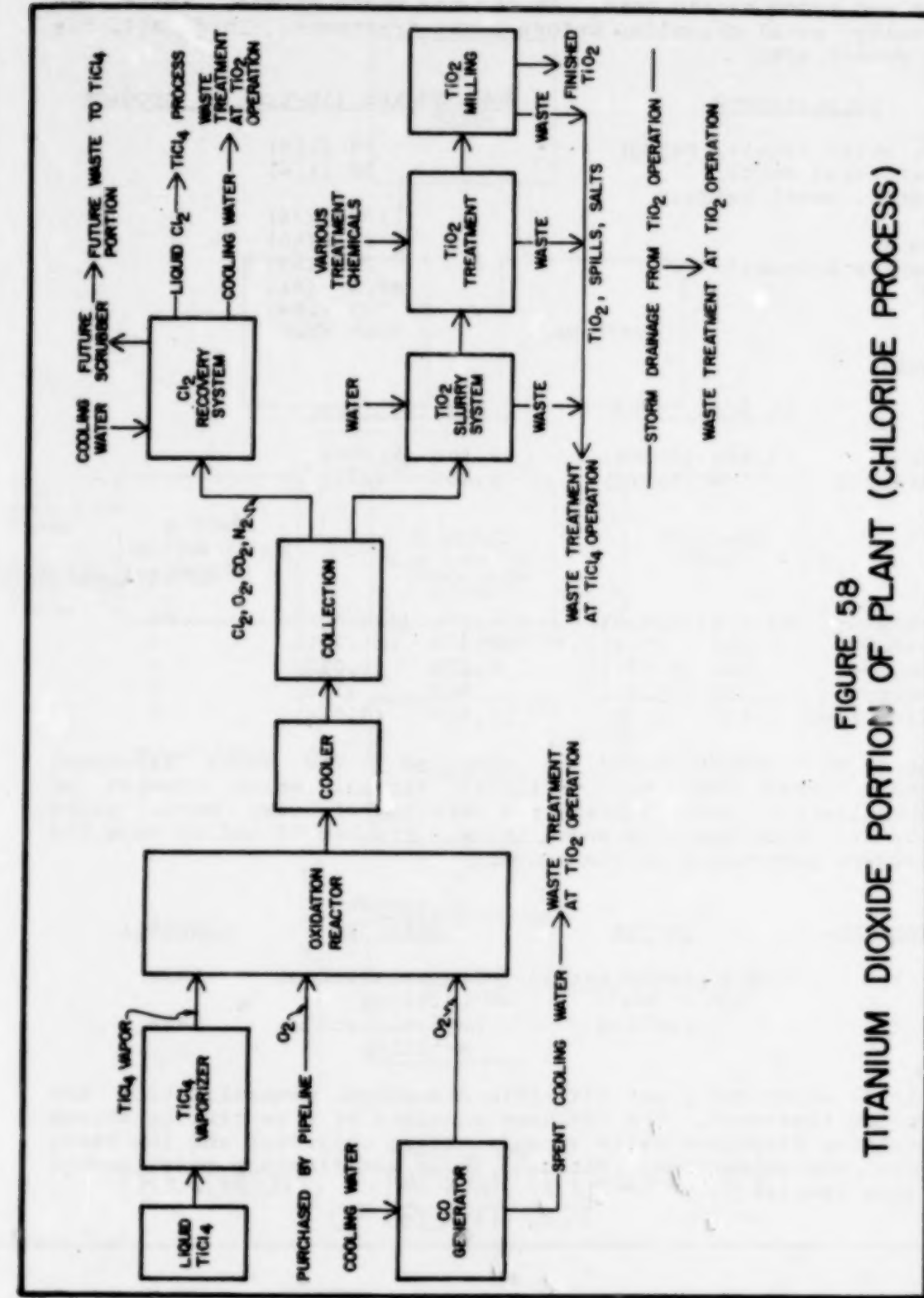
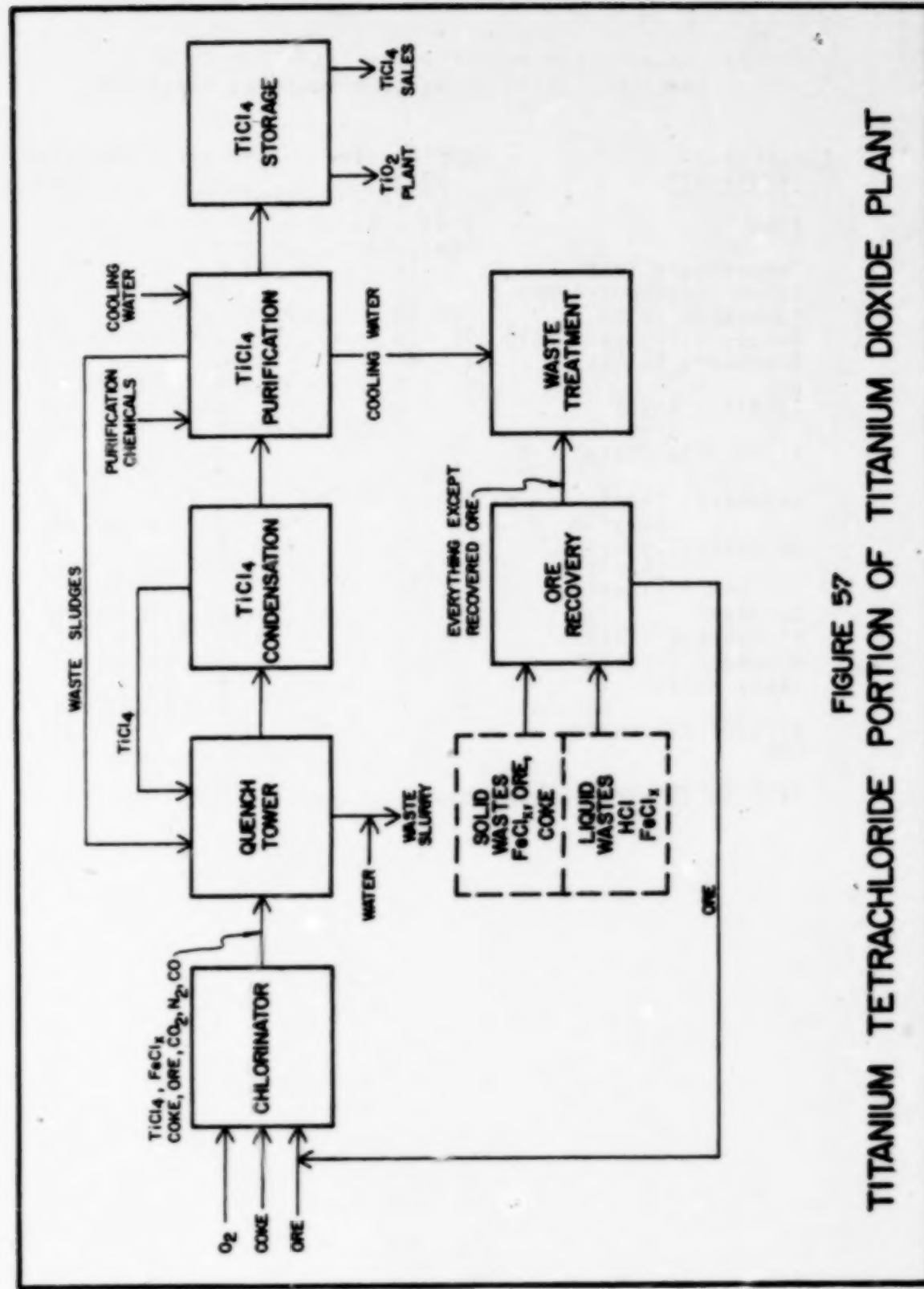
Parameter*	Intake	Effluent
Flow cu m/day (MGD)	Not Measured	11,350 (3.0)
Temperature, °C	13	26.5
Color (apparent - APHA std.)	40	40
Turbidity (FTU)	10	15
Conductivity (as NaCl)	17,500	18,000
Suspended Solids	10	5
pH	7.5	7.43
Acidity: Total	-	-
Free	-	-
Alkalinity: (Total) P(CaCO <sub>3</sub> )	0	0
T( " )	93	91
Hardness: Total(CaCO <sub>3</sub> )	3,300	3,200
Calcium(CaCO <sub>3</sub> )	600	590
Halogens: Chlorine	-	-
Chloride	10,000	10,000
Fluoride	-	-
Sulfate	1,500	1,500
Phosphates (Ortho)	0.70	0.68
Nitrate, N	0.24	0.26
Heavy Metals: Iron	0.28	0.32
Chromate	-	-
Oxygen (Dissolved)	-	-
Sulfite	1	1
COD	-	-

\*All units mg/l unless otherwise specified.

TABLE 31. In-Plant Water Streams at Plant 141

Parameter*	Well Intake Water	Sump to Ponds	Evaporation Pond
Flow	Unable to measure	-	-
Temperature (°C)	19	24.6	17.5
Color (Apparent-APHA)	100	0	35
Turbidity (FTU)	35	10	10
Conductivity (as NaCl)	410	360	790
Suspended Solids	40	4700	0
pH	7.0	8.5	7.7
Acidity: Total	0	0	0
Free	0	0	0
Alkalinity (Total) P	0	0	0
T	475	120	105
Hardness: Total	410	250	500
Calcium	275	112	400
Halogens: Chlorine	0	0	0
Chloride	18.5	20	22.5
Fluoride	0.35	0.6	0.77
Sulfate	78	340	680
Phosphates (Total)	1.6	0.64	0.12
Nitrogen (Total)	0.03	0.18	0
Heavy Metals: Iron	18	9	4
Chromate	0	0.16	0.03
Oxygen (Dissolved)	5.3	5.5	7.9
COD	25	575	70

\*All units mg/l unless otherwise specified.



The raw wastes from plant 009 consist of heavy metal salts, waste coke and hydrochloric acid. In the raw waste stream, these are actually metal chlorides before waste treatment. In detail, the raw wastes are:

Constituents	Ave. kg/kkg (lb/ton) of product	
Iron salts (equiv. Fe <sub>2</sub> O <sub>3</sub> )	58	(116)
Other metal salts (equiv. metal oxides)	58	(116)
Ore	138	(276)
Coke	23	(46)
Titanium hydroxide	29	(58)
TiO <sub>2</sub>	40.5	(81)
HCl	227	(454)

Input:

	cu m/day (mgd)	l/kkg (gal/ton)
Lake	11,500 (0.304)	17,100 (4,100)
Municipal	76 (0.020)	1,130 (270)

Use:

			Percent Recycled
Cooling	58,700 (15.5)	876,000 (210,000)	93
Process	6,060 (1.6)	90,500 (21,700)	0
Cleanup	284 (0.075)	4,220 (1,010)	0
Sanitary	38 (0.01)	560 (140)	0
Boiler feed	834 (0.22)	12,500 (3,000)	0

Most of the cooling water is recycled. The waste treatment methods used on the effluent stream, which consist of neutralization, precipitation and settling of heavy metal salts prior to discharge, are shown below. Figures 59 and 60 show the treatment processing at plant 009.

Stream No.	Source	Treatment Methods	Disposal
1	TiCl <sub>4</sub> precipitation	Neutralization, settling	Lake
2	Cooling	Neutralization, settling	Lake

Table 32 shows the plant 009 effluents after neutralization and settling treatment. The effluent consists of a neutral pH stream containing dissolved salts (mostly sodium chloride) and low heavy metals concentrations. Table 33 shows verification measurements at this facility.

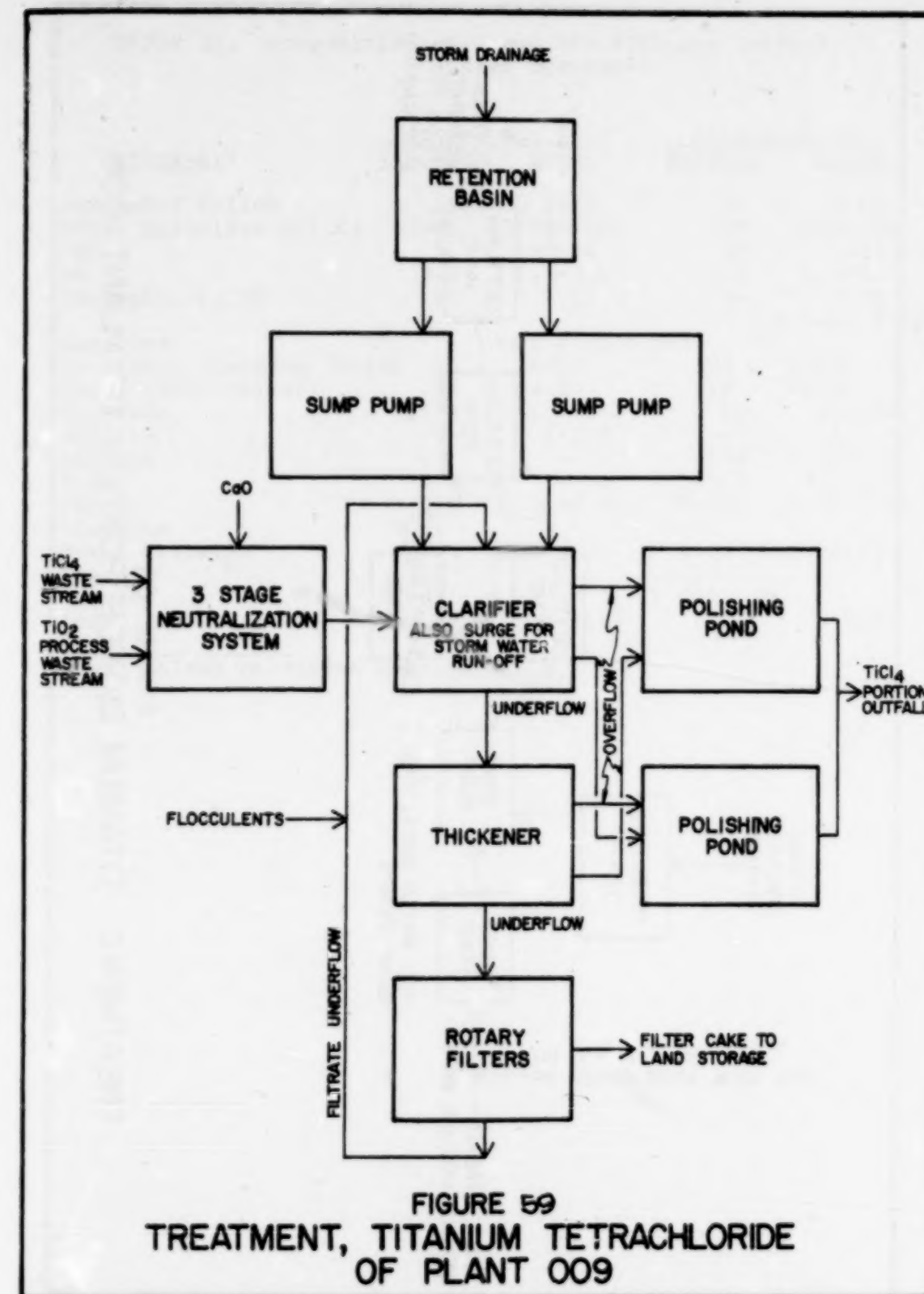


FIGURE 59  
TREATMENT, TITANIUM TETRACHLORIDE  
OF PLANT 009



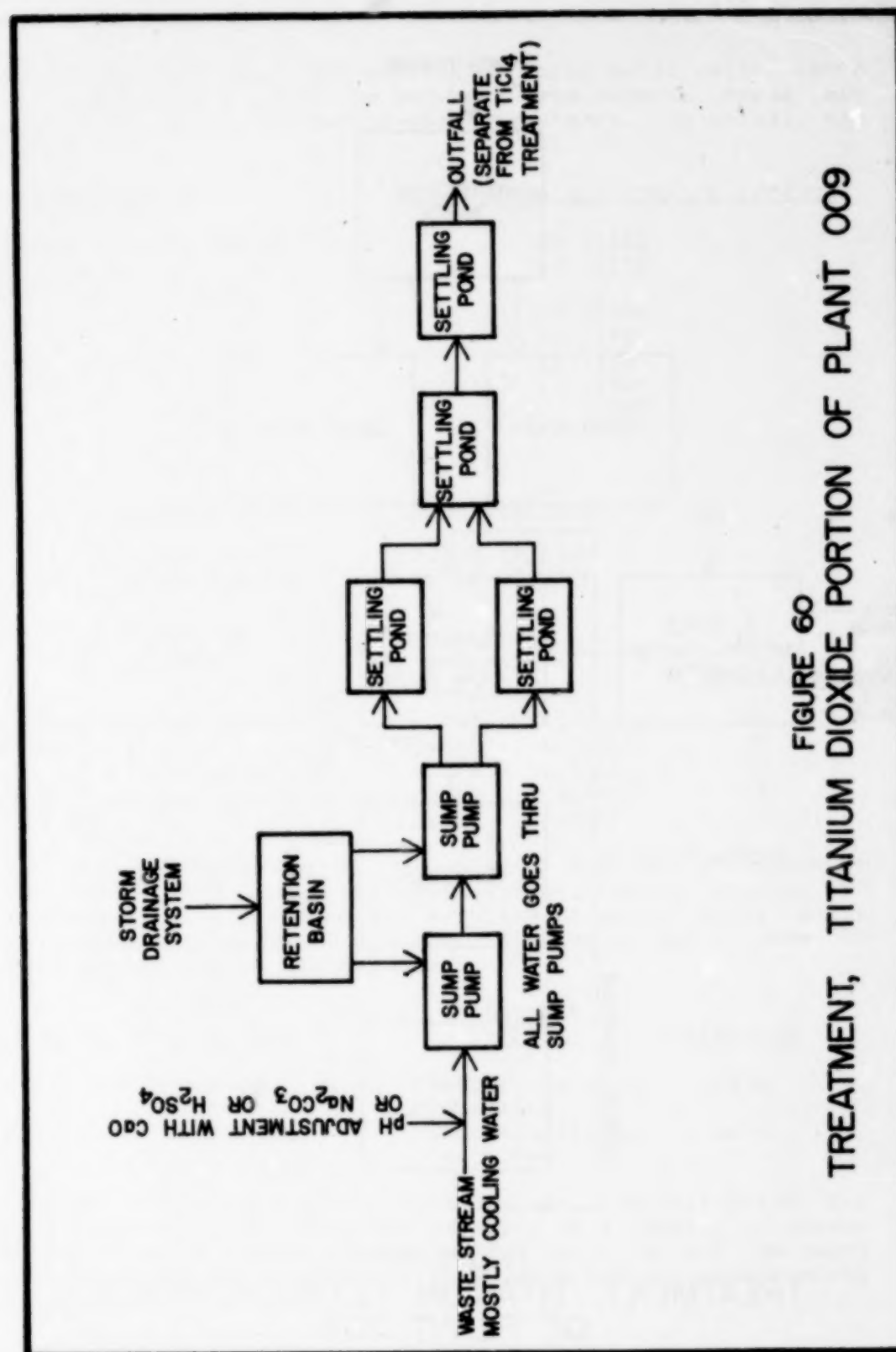


FIGURE 60  
TREATMENT, TITANIUM DIOXIDE PORTION OF PLANT 009

TABLE 32. Composition of Plant 009 Effluent Streams After Treatment

Parameter*	Stream No. 1		Stream No. 2	
	Average	Range	Average	Range
Suspended Solids	18	1-50	15	0-40
Total Dissolved Solids	3300	1500-4500	300	180-900
COD	50	40-90	20	5-45
pH	7.8	6.0-9.0	6.8	6.0-9.0
Temperature, °C	16	7-27	16	2-32
			(Ambient Temp.)	
Organics		None were found		
Turbidity (Jackson Units)	20	10-80	20	10-50
Color (APHA Units)	10	10-20	10	10-20
Chloride	1650	750-2050	50	70-100
Sulfate	--	1-2.5	--	1-2.5
Sulfate	--	--	150	90-450
Iron	0.2	0-3.0	0.2	0.1-1.0
Copper	0.015	0.01-0.03	0.015	0.01-0.03
Chromate	0.01		0.01	
Total Chromium	0.05	0.01-0.15	0.05	0.01-0.15
Arsenic	0.02		0.02	
Mercury	0.001		0.001	
Lead	0.14	0.1-0.19	0.02	0.02

\*mg/l unless otherwise specified

TABLE 33. Verification Data of Plant 009

Parameter*	Lake Intake Water	Effluent Stream #1	Effluent Stream #2
Flow, cu m/day (MGD)	3650 (0.964)	6060 (1.60)	2240 (0.590)
Temperature, °C	.9	16	26.5
Color (APHA Units)	100	140	90
Turbidity (FTU)	35	35	30
Conductivity	100 (NaCl)	2100 (NaCl)	170 (NaCl)
Suspended Solids	25.0	10	30
pH	7.9	7.6	6.85
Acidity: Total	N/A	N/A	0 (CaCO <sub>3</sub> )
Free	N/A	N/A	0 (CaCO <sub>3</sub> )
Alkalinity (Total) P	0 (CaCO <sub>3</sub> )	0 (CaCO <sub>3</sub> )	0 (CaCO <sub>3</sub> )
T	93 (CaCO <sub>3</sub> )	22 (CaCO <sub>3</sub> )	28 (CaCO <sub>3</sub> )
Hardness: Total	129 (CaCO <sub>3</sub> )	2600 (CaCO <sub>3</sub> )	185 (CaCO <sub>3</sub> )
Calcium	97 (CaCO <sub>3</sub> )	1920 (CaCO <sub>3</sub> )	139 (CaCO <sub>3</sub> )
Halogens: Chlorine	0	0	0
Chloride	36.5	2250	49.5
Fluoride	0	0.3	0.25
Sulfate	32.0	240	175
Phosphates (Total)	1.4	0.025	0.225
Nitrogen (Total)	0.24	0.14	1.3
Heavy Metals:			
Iron	0.225	1.6	0.4
Chromate	0 (Cr+6)	0 (Cr+6)	0 (Cr+6)
Oxygen (Dissolved)	10.8	9.0	6.2

\*mg/l unless otherwise specified

## b) Sulfate process

For the sulfate process, we have examined information on all the existing facilities in the United States. The following description lists the raw wastes and waste segregation practices normally used by the industry and describes planned improved treatments.

In the sulfate process, ground ilmenite ore is digested with concentrated sulfuric acid at relatively high temperature. The acid used is normally about 150 percent of the weight of the ore. In some cases, small amounts of antimony trioxide are also added. The resulting sulfates of titanium and iron are then leached from the reaction mass with water, and any ferric salts present are then reduced to ferrous by treatment with iron scrap to prevent coloration of the final titanium dioxide product.

After these operations, the resulting solutions are clarified, cooled and sent to a vacuum crystallizer. There, ferrous sulfate crystallizes out and is then separated from the mother liquor by centrifugation. This material is either sold or disposed of as a solid waste.

The mother liquor is then clarified by filtration after addition of filter aid and is further concentrated by vacuum evaporation. Seed crystals or other nucleating agents are added, and the concentrated liquor is then treated with steam to hydrolyze the titanyl sulfate present. The resulting precipitate is collected by filtration, washed several times and then calcined to yield titanium dioxide. The calcined product is ground, quenched and dispersed in water. The coarse products are separated in a thickener to which caustic soda is added to maintain a constant pH. These coarse particles are reground and further processed to yield a purer product.

Table 34 gives a generalized listing of the raw wastes from titanium dioxide manufacture by the sulfate process. Data in this table are in a form applicable to the effluent from any of the five existing sulfate process plants. Each of these five facilities have slightly different raw wastes due to differences in compositions of the raw ores. Table 35 lists typical ores used in U.S. manufacture of titania, with the Adirondack and Australian Ilmenites being typical of ores used with the sulfate process.

Discussion of water use and treatment will be based on one facility, chosen from the five plants. The specific facility used for this modeling discussion is plant 122. A general waste treatment flow chart for this facility is presented in Figure 61 and generalized water usage is:

TABLE 34. Sulfate Process Waste Streams --  
Titanium Dioxide Manufacture

1. Dissolving and Filtration	Ore and scrap iron plus flocculants $H_2SO_4$ Organic Carbon	0.07 x total ore and scrap iron discharged 0.0016 x ore 0.0004 x ore plus 0.1 x C in ore
2. Copperas (if produced)	$FeSO_4 \cdot 7H_2O$ (as Fe)	( $Fe^{+2} + 1.50 Fe^{+3}$ ) in ore minus 0.33 x $TiO_2$ in ore
3. Strong Acid	Total Sulfate $FeSO_4$ (as Fe)  $H_2SO_4$ Other ore impurities $TiO_2$ Organic Carbon	1.76 x iron in copperas 0.67 x (iron in ore minus iron in copperas) 1.07 x ore 0.67 x impurities in ore 0.03 x $TiO_2$ in ore 0.0022 x ore plus 0.81 x C in ore
4. Weak Acid	$FeSO_4$ (as Fe)  $H_2SO_4$ (Total)  Other ore impurities $TiO_2$ Organic Carbon	0.33 x (iron in ore minus iron in copperas) 0.53 x ore plus 0.25 x $TiO_2$ in ore 0.33 x impurities in ore 0.02 x $TiO_2$ in ore 0.00025 x ore plus 0.09 x C in ore
5. Vent and Kiln Scrubbing	$H_2SO_4$	0.01 in ore
6. $TiO_2$ Losses	$TiO_2$ $Na_2SO_4$	0.016 x $TiO_2$ in ore 0.03 x $TiO_2$ in ore

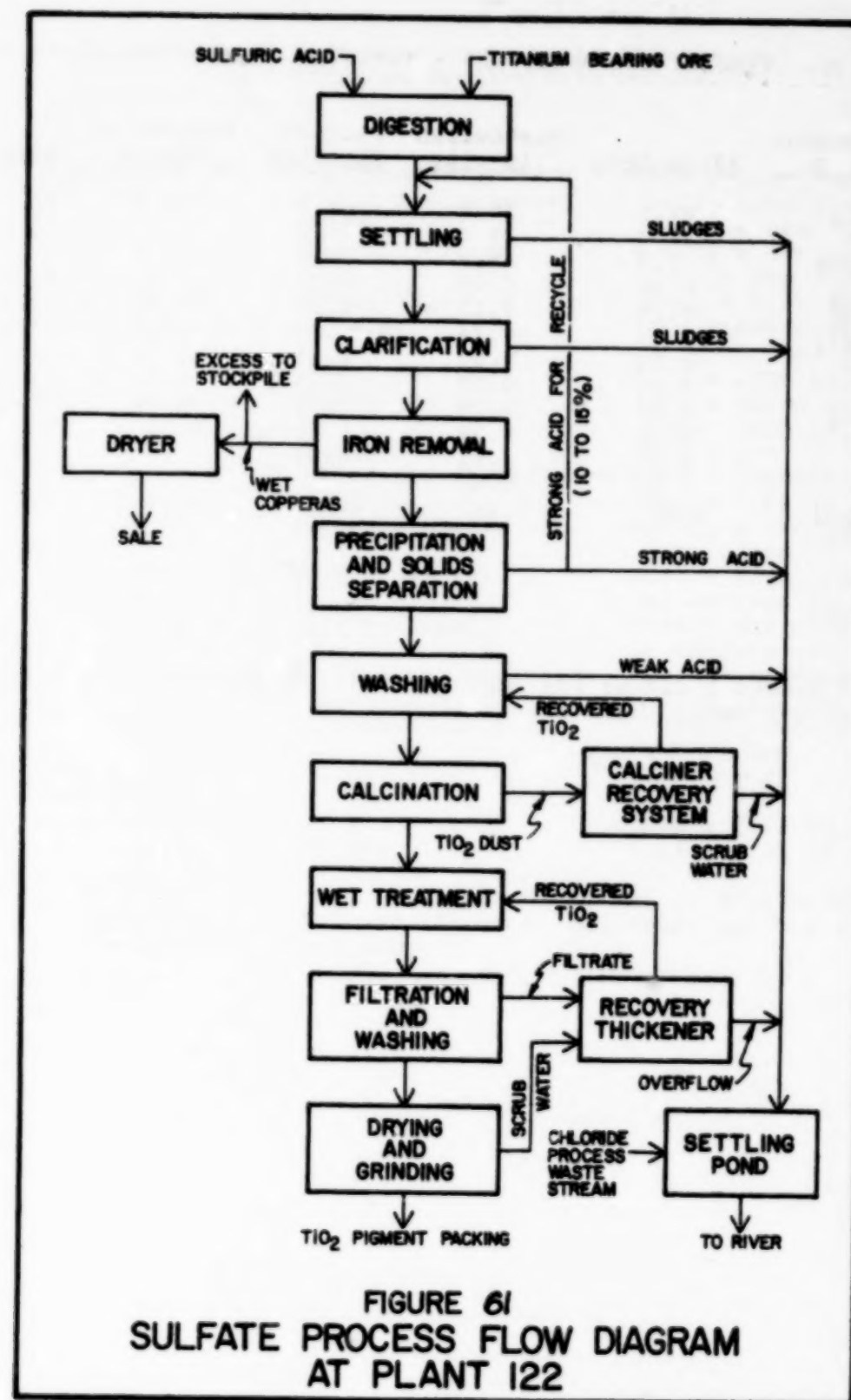
Note: Effluents also contain traces of Pb and Cu from process equipment. Silica and zircon do not react and are discharged with the sludge.

TABLE 35. Typical Ore Analyses\* - Titanium Dioxide Manufacture

Constituent (Wt. %)	Adirondack	Australian Ilmenite	Florida Ilmenite	Australian Rutile	Slag
$TiO_2$	44.5	55.4	64.0	96.3	71.0
FeO	38.0	23.8	3.2		10.9
$Fe_2O_3$	5.8	16.9	26.9	0.28	
$P_2O_5$	0.04	0.08	0.21	0.03	0.01
$V_2O_5$	0.14	0.17	0.13	0.56	0.5
$Al_2O_3$	1.79	0.94	1.5	0.39	5.7
CaO	0.58	0.02	0.13	0.01	1.0
MgO	2.14	0.27	0.35	0.05	5.0
$SiO_2$	2.48	0.15	0.3	0.28	5.0
MnO	0.50	0.72	1.35	0.01	0.3
S	0.17	0.01	0.09		0.09
Co	0.02	0.11			
$Cr_2O_3$	0.01	0.14	0.10	0.20	0.2
$ZrO_2$			0.07	0.6	
Fe					0.5
C			0.27		
$NbO_2$			0.11	0.30	
H			0.27	0.02	

\*Blank spaces indicate low impurity level or absence of reliable analytical data. Data from reference 14.





Type	cu m/kg of Product (gal/ton)	Recycle
Cooling	284 (68,000) brackish	0 percent
Cooling	83.6 (20,000) fresh	90 percent
Process	100 (24,000)	2 percent
Boiler feed	16.7 (4,000)	30 percent

Currently, all of the process water used is fed to a settling pond to remove suspended materials and is then discharged. The process water discharged is from two streams, one from a solids separation part of the process which contains strong (18-22 percent) acid and a second weak acid stream coming from other parts of the process. Both streams are currently mixed before treatment.

In the treatment of wastes, the best approach would be to segregate these two streams and attempt to recover acid values and/or ferrous sulfate from the more acidic stream, while applying neutralization procedures to the other. Considering the strong acid stream first, a possible recovery treatment is first to partially evaporate the waste to effect further precipitation of ferrous sulfate and other metal salts which could be recovered by filtration after cooling. The remaining solution could be further concentrated for other use or recycled to the process.

The weak acid stream, which does not contain sufficient metal or acid values to justify recovery, would be oxidized to convert ferrous salts to the ferric state and then treated with lime to precipitate heavy metals and adjust for pH to contain about 2000 mg/l dissolved  $\text{CaCO}_3$ .

One advantage to this scheme is the possibility of further processing the heavy metal salts recovered by acid concentration. These could possibly be further processed to recover vanadium values, among others. It may be noted that the above-mentioned scheme is a combination of two treatment approaches. The method involving total neutralization and settling is currently being installed at the plant 122 to treat all of the waste streams. Table 36 lists some information on this treatment process.

Effluents from four titanium dioxide sulfate process facilities are listed in Table 37. None of these have discharge pH's in the 6.0-9.0 range for all streams, and all contain 3000 mg/l dissolved solids. In some cases, strong acid streams are currently segregated and this material, in one case, is disposed of by ocean dumping. The neutralization procedure, along with a possible scheme for some acid recovery was discussed earlier in this section.

For the sulfate process, an alternate treatment may consist of raw ore enrichment to remove much of the iron present before the raw material is used in the process. One such potential process

TABLE 36. Future Treatment at Plant 122

<u>Methods</u>	<u>Estimated Installation Time</u>	<u>Estimated Performance</u>
Neutralization of acid to $\text{CaSO}_4$ and oxidation of iron, and remove for sale or stockpile (as ferrous sulfate) of process wastes and cooling water	22 mos	Reduce C.O.D to Nil Reduce acidity to Nil Reduce Fe, Mn, V, and Cr to Nil TDS 50 mg/l
Additional settling ponds for cooling waters	22 mos	Reduction of suspended solids formed due to neutralization by 95%

TABLE 37. Partial Discharge Data from  $\text{TiO}_2$  Sulfate Plants (1)

<u>Parameter*</u>	<u>Plant 142 (2)</u> <u>Streams</u>		<u>Plant 046 Streams (3)</u>			<u>Plant 122</u> <u>Streams</u>			<u>Plant</u> <u>008</u>
	<u>No. 1</u>	<u>No. 2</u>	<u>No. 1</u>	<u>No. 2</u>	<u>No. 3</u>	<u>No. 1</u>	<u>No. 2</u>	<u>No. 3</u>	<u>No. 1</u>
BOD <sub>5</sub>	10	3	6	3	--	--	0.3	0.5	--
COD	71	145	--	--	--	287	42	27	--
pH	8.0	1.2	6.5	5.6	--	1.0	2.6	5.0	5 min
Alkalinity	220	--	--	--	--	--	--	--	--
Total Dis- solved Solids	1660	22,371	15,316	21,300	14,000	15,400	3,000	2,700	5,000
Iron	0.02	823	0.5	1.7	31,000	1,000	45	15	100
Sulfate	1,170	12,377	1,617	1,378	131,000	6,800	187	125	--
Chloride	51.5	105	6,394	7,900	--	625	2,480	2,830	--
Acidity	--	11,435	36	--	--	20,000	160	1000	--
Flow, cu m/day (MGD)	10,200	Combined	20,000	123,400	6,100	20,000	40,900	30,300	
	(2.7)	--	(5.5)	(32.6)	(1.6)	(5.5)	(10.8)	(8.0)	

(1) One plant of one manufacturer is not listed here. Data on titanium dioxide and chromate concentrations were provided.

(2) The corporation owning this facility is currently developing a process for recovery and recycle of the sulfuric acid used. This process is still under testing on the pilot plant scale.

(3) This plant barges its strong acid wastes out to sea for disposal. This method of disposal of highly acid wastes containing large amounts of dissolved heavy metals is not considered satisfactory. Effluent No. 3 is the available data on material dumped at sea.

\*mg/l unless otherwise specified



under development at the U.S. Bureau of Mines Reno Research Center involves the smelting of ilmenite ( $\text{FeTiO}_3$ ) with coal and sodium borate-titanate slag which contains 40 weight percent titanium dioxide and 0.2 weight percent iron. Over 99 percent of the titanium in the ore is recovered in the slag, while about 90 percent of the iron present is converted to the elemental form. After separation of the iron from the slag, air or oxygen is blown into the molten slag to oxidize the titanium to the tetravalent form which is readily soluble in acid. The molten slag is water quenched and leached in hot water to yield a sodium titanate residue (70 - 90 weight percent  $\text{TiO}_2$ ) in a sodium borate solution. The recovered titanate can then be used in the sulfate process.

Sodium borate in solution is recovered by crystallization and can be recycled to the smelting step. Use of this procedure to provide a sodium titanate feed for the sulfate process eliminates the generation of large amounts of iron sulfate and the inherent problems related to its disposal.

Other methods of ore enrichment under development have been alluded to by the various sulfate process titanium dioxide producers, but details have not been made available.

Substitution of sodium titanate for ilmenite as a sulfate process raw material would lead to a sulfate - bisulfate by-product which could be recovered by crystallization (as is done with ferrous sulfate) for sale. This would eliminate much of the heavy metal salt discharge problems with the sulfate process and also solve the problem of acidic discharges via recovery of a low grade sodium bisulfate by-product for sale or other use.

This approach may prove to be a superior approach to either the neutralization scheme or the acid recovery techniques mentioned earlier. The economics of the above mentioned possible sulfate process modification have not yet been reported. A more detailed evaluation of this possible process must await such an economic presentation.

#### VERIFICATION SAMPLING AND ANALYTICAL METHODS

##### Sampling Operations

Two teams of two men each were assigned to the field sampling and measurements operations. Each of the teams was equipped with a station wagon and a 4.7-meter trailer outfitted as a mobile water testing laboratory. The visit of a team to each facility was preceded by a visit to the plant by one of the senior engineers on the project team. During this visit, effluent streams and potential sampling sites were determined and approximate expected stream compositions were established.

The duties of the field team visiting the plant included measurement of flow rate and collection of samples at each designated sampling site. Methods used to determine flow rates varied from stream to stream, but included: (1) Use of existing weirs or installed flow meters; (2) Use of current meter plus dimensional measurements; (3) Direct collection of small outfall streams, with volumetric measurement related to duration of collection; (4) Use of dye tracer to give velocity measurement (plus dimensional measurements).

Since many of the streams of interest could not be approached, the wastes contained therein were sampled after having mixed with one or more other streams.

For most effluent sampling sites, four one-liter samples were taken (one per hour) over a four-hour duration. These samples were then mixed to give a four-liter composite sample. One four-liter grab sample was taken of the water supply to the plant. At the end of the day, a four-liter grab sample was taken at each sampling site (and of the water supply) for backup.

One-half of the four-liter composite sample was used for analyses and tests in the field laboratory. The remaining two liters of composite sample were divided into several samples, some of which were acid-stabilized and transported to an analytical lab for further testing. The sample was split with the plant where it was collected when requested by plant personnel.

The results obtained by the use of the field transportable test methods were, in general, quite reliable. As a routine matter, however, standard test samples were inserted into the analytical program to allow some estimate of the validity of the results reported from the field. The unlabeled standard samples were made up from EPA Reference Samples and presented to the analytical personnel without obvious identification.

The analysis of the samples from various process and discharge streams has been a somewhat complex procedure. This is due, primarily, to the extraordinary variation in flow rates, concentration of solutes and (in particular) the extremely wide range of suspended solids which was encountered.

Pretreatments in the field for the various types of samples were:

- (1) Suspended and dissolved solids - none;
- (2) Metal ion analysis - addition of 5 ml of concentrated nitric acid per liter of sample;
- (3) COD analysis - used immediately in the dichromate reflux apparatus or treated with 1.0 N sulfuric acid;
- (4) Nitrogen analysis - used immediately or treated with mercuric chloride for stabilization;



- (5) Phosphorus - addition of 40 mg. of mercuric chloride per liter; and  
(6) Fluoride - none.

The analytical methods used are those described in EPA's Methods for Chemical Analysis of Water and Wastes, 1971.

## SECTION VI

### SELECTION OF POLLUTANT PARAMETERS

The waste water characterization detailed in the previous Section has been reviewed to determine what waste water constituents are present in significant quantities from the various product subcategories. The criterion used in the selection of pollutant parameters for each subcategory include:

- a) Sufficient data is available with regard to the quantities of a pollutant in the raw waste load as well as its treatability by various waste water treatment systems.
- b) The pollutant is generally present in the raw waste load in quantities sufficient to cause deleterious effects on the environment.
- c) There is demonstrated technology to practicably and economically reduce the concentration of the pollutant.

The following is a discussion of those pollutant parameters which have been selected as the subject of effluent limitations. They have only been selected for those chemical subcategories in which they are generally present in significant quantities.

#### pH

The term pH is a logarithmic expression of the concentration of hydrogen ions. At a pH of 7, the hydrogen and hydroxyl ion concentrations are essentially equal and the water is neutral. Lower pH values indicate acidity while higher values indicate alkalinity. The relationship between pH and acidity or alkalinity is not necessarily linear or direct.

Waters with a pH below 6.0 are corrosive to water works structures, distribution lines, and household plumbing fixtures and can thus add such constituents to drinking water as iron, copper, zinc, cadmium and lead. The hydrogen ion concentration can affect the "taste" of the water. At a low pH water tastes "sour". The bactericidal effect of chlorine is weakened as the pH increases, and it is advantageous to keep the pH close to 7. This is very significant for providing safe drinking water.

Extremes of pH or rapid pH changes can exert stress conditions or kill aquatic life outright. Dead fish, associated algal blooms, and foul stench are aesthetic liabilities of any waterway. Even moderate changes from "acceptable" criteria limits of pH are deleterious to some species. The relative toxicity to aquatic life of many materials is increased by changes in the water pH. Metalocyanide complexes can increase a thousand-fold in toxicity with a drop of 1.5 pH units. The availability of many nutrient

substances varies with the alkalinity and acidity. Ammonia is more lethal with a higher pH.

The lacrimal fluid of the human eye has a pH of approximately 7.0 and a deviation of 0.1 pH unit from the norm may result in eye irritation for the swimmer. Appreciable irritation will cause severe pain.

#### Total Suspended Solids

Suspended solids include both organic and inorganic materials. The inorganic components include sand, silt, and clay. The organic fraction includes such materials as grease, oil, tar, animal and vegetable fats, various fibers, sawdust, hair, and various materials from sewers. These solids may settle out rapidly and bottom deposits are often a mixture of both organic and inorganic solids. They adversely affect fisheries by covering the bottom of the stream or lake with a blanket of material that destroys the fish-food bottom fauna or the spawning ground of fish. Deposits containing organic materials may deplete bottom oxygen supplies and produce hydrogen sulfide, carbon dioxide, methane, and other noxious gases.

In raw water sources for domestic use, state and regional agencies generally specify that suspended solids in streams shall not be present in sufficient concentration to be objectionable or to interfere with normal treatment processes. Suspended solids in water may interfere with many industrial processes, and cause foaming in boilers, or encrustations on equipment exposed to water, especially as the temperature rises. Suspended solids are undesirable in water for textile industries; paper and pulp; beverages; dairy products; laundries; dyeing; photography; cooling systems, and power plants. Suspended particles also serve as a transport mechanism for pesticides and other substances which are readily sorbed into or onto clay particles.

Solids may be suspended in water for a time, and then settle to the bed of the stream or lake. These settleable solids discharged with man's wastes may be inert, slowly biodegradable materials, or rapidly decomposable substances. While in suspension, they increase the turbidity of the water, reduce light penetration and impair the photosynthetic activity of aquatic plants.

Solids in suspension are aesthetically displeasing. When they settle to form sludge deposits on the stream or lake bed, they are often much more damaging to the life in water, and they retain the capacity to displease the senses. Solids, when transformed to sludge deposits, may do a variety of damaging things, including blanketing the stream or lake bed and thereby destroying the living spaces for those benthic organisms that would otherwise occupy the habitat. When of an organic and

therefore decomposable nature, solids use a portion or all of the dissolved oxygen available in the area. Organic materials also serve as a seemingly inexhaustible food source for sludgeworms and associated organisms.

Turbidity is principally a measure of the light absorbing properties of suspended solids. It is frequently used as a substitute method of quickly estimating the total suspended solids when the concentration is relatively low.

#### Cyanide

Cyanides in water derive their toxicity primarily from undissolved hydrogen cyanide (HCN) rather than from the cyanide ion (CN<sup>-</sup>). HCN dissociates in water into H<sup>+</sup> and CN<sup>-</sup> in a pH-dependent reaction. At a pH of 7 or below, less than 1 percent of the cyanide is present as CN<sup>-</sup>; at a pH of 8, 6.7 percent; at a pH of 9, 42 percent; and at a pH of 10, 87 percent of the cyanide is dissociated. The toxicity of cyanides is also increased by increases in temperature and reductions in oxygen tensions. A temperature rise of 10°C produced a two- to three-fold increase in the rate of the lethal action of cyanide.

Cyanide has been shown to be poisonous to humans, and amounts over 18 mg/l can have adverse effects. A single dose of 6 mg/l, about 50-60 mg, is reported to be fatal.

Trout and other aquatic organisms are extremely sensitive to cyanide. Amounts as small as 0.1 mg/l can kill them. Certain metals, such as nickel, may complex with cyanide to reduce lethality especially at higher pH values, but zinc and cadmium cyanide complexes are exceedingly toxic.

When fish are poisoned by cyanide, the gills become considerably brighter in color than those of normal fish, owing to the inhibition by cyanide of the oxidase responsible for oxygen transfer from the blood to the tissues.

#### Chromium

Chromium, in its various valence states, is hazardous to man. It can produce lung tumors when inhaled and induces skin sensitizations. Large doses of chromates have corrosive effects on the intestinal tract and can cause inflammation of the kidneys. Levels of chromate ion that have no effect on man appear to be so low as to prohibit determination to date.

The toxicity of chromium salts toward aquatic life varies widely with the species, temperature, pH, valence of the chromium, and synergistic or antagonistic effects, especially that of hardness. Fish are relatively tolerant of chromium salts, but fish food



organisms and other lower forms of aquatic life are extremely sensitive. Chromium also inhibits the growth of algae.

In some agricultural crops, chromium can cause reduced growth or death of the crop. Adverse effects of low concentrations of chromium on corn, tobacco and sugar beets have been documented.

#### Chemical Oxygen Demand

Certain waste water components are subject to aerobic biochemical degradation in the receiving stream. The chemical oxygen demand is a gross measurement of organic and inorganic material as well as other oxygen-demanding material which could be detrimental to the oxygen content of the receiving water.

#### Iron

The presence of iron in water causes taste and turbidity problems. It has been shown to be harmful to fish and plants in varying concentrations. Ferric hydroxide has been known to cause detrimental effects to plankton.

#### Lead

The presence of lead may be a problem in receiving waters. Various oysters and lobsters are known to be adversely effected when exposed to lead in concentrations less than 0.5 mg/l. Lead poisoning in humans has been reported to have been caused by drinking water containing less than 0.1 mg/l lead.

#### Mercury

Mercury has been shown to be deleterious to the environment in low concentrations. Many aquatic organisms are adversely affected by mercury concentrations of less than 0.01 mg/l.

#### Total Organic Carbon

Soluble organics may cause utilization or depletion of dissolved oxygen by the activity of aerobic bacteria. They may also impart undesirable tastes and odors to a water supply. For example, phenolics are a special nuisance in drinking water supply, particularly after chlorination, because of the very low concentrations (less than 0.002 mg/l) which result in taste and odor detection.

The quantity of soluble organics can be measured as BOD, COD or TOC (Total Organic Carbon). However, each of these parameters will measure differing amounts of soluble organics. For example, many organic compounds which are dichromate oxidizable (COD) are not biochemically oxidizable (BOD). Also, many inorganic substances such as sulfides, nitrites, etc., are oxidized by

dichromate (COD) which may be misleading when estimating the organic content of the waste water. The total organic carbon determination oxidizes the carbon atoms of organic molecules to carbon dioxide, and measures the amount of carbon dioxide quantitatively. It lacks the many variables present in the COD and BOD analyses, resulting in more reliable and reproducible results for organic determinations.

In general, other pollutant parameters have not been selected because they are present in relatively small quantities. There are a few notable exceptions, however. Dissolved salts, such as chlorides and sulfates, are often present in large quantities. Treatment technologies to reduce or remove these constituents may be expensive and in many cases the costs are prohibitive at this time.

Titanium dioxide manufacture generates a waste stream containing many types of metal ions. Treatment and removal of iron will coincidentally remove other metals to acceptable levels. Therefore, other waste water constituents have not been the subject of effluent guidelines, even though they may be present in large quantities.



## SECTION VII

### CONTROL AND TREATMENT TECHNOLOGY

Alternative control and treatment technologies for each chemical subcategory are discussed in detail on the following pages.

#### SPECIFIC CONTROL AND TREATMENT PRACTICES IN THE INDUSTRY

##### Aluminum Chloride

Direct chlorination of aluminum to produce aluminum chloride is a relatively simple process. Plants are small (9 to 18 metric tons/day). There is no process water involved, nor usually any cooling water. The only source of water wastes is from equipment used to treat air-borne wastes such as aluminum chloride dust around the packing station and aluminum chloride and chlorine from the air-cooled condensers.

In some plants, run on the aluminum-rich side (white or gray aluminum chloride), there is very little chlorine in the discharge from the air-cooled condenser. Also, the gas volume from the condenser is such that only a very small quantity of aluminum chloride is discharged. In such plants there may be no air pollution control provision. One exemplary plant operates in this fashion. In plants operating on the chlorine-rich side (yellow aluminum chloride), water scrubbing of the air condenser discharge gases is needed.

At least three practicable, economically feasible, and low energy air pollution control approaches are available:

- (1) No air or gas treatment for gray or white aluminum chloride.
- (2) Gas scrubbing and sale of scrubber wastes. This approach is taken by an exemplary plant of this study.
- (3) Gas scrubbing followed by chemical treatment to precipitate aluminum hydroxide and convert chlorine to sodium chloride. Technology available from the chlor-alkali and titanium dioxide chloride process may be applied.

##### Aluminum Sulfate

Current typical treatment involves use of a settling pond to remove muds followed by neutralization of residual sulfuric acid prior to discharge.

Two exemplary plants (049 and 063) have closed loop waste-water systems. Suspended solids are removed in settling vessels and ponds and the clear overflow is returned to the manufacturing process.

TABLE 3B. Summary of BPCTCA and BATEA

Chemical	BPCTCA Guideline	Best Practicable Control Technology Currently Available BPCTCA	BATEA Guideline	Best Available Technology Economically Achievable BATEA
Aluminum Chloride (Anhydrous)	No discharge of pollutants in process waste waters	(1) No water scrubbers for white or gray aluminum chloride production (2) For yellow aluminum chloride pro- duction, gas scrubbing and sale of scrubber wastes as aluminum chloride solution; or (3) Gas scrubbing followed by chemical treatment to precipitate aluminum hydroxide and and recycle	Same as BPCTCA	Same as BPCTCA
Aluminum Sulfate	No discharge of pollutants in process waste waters	(1) Settling pond and reuse	Same as BPCTCA	Same as BPCTCA
Calcium Carbide	No discharge of pollutants in process waste waters	(1) Dry dust collection system	Same as BPCTCA	Same as BPCTCA
Hydrochloric Acid Chlorine Burning	No discharge of pollutants in process waste water	(1) Acid containment and isolation with centralized collection of acid wastes; and reuse	Same as BPCTCA	Same as BPCTCA
Hydrofluoric Acid	No discharge of pollutants in process waste waters	(1) Acid containment and isolation; and reuse	Same as BPCTCA	Same as BPCTCA
Sodium Bicarbonate	No discharge of pollutants in process waste water	(1) Evaporation and product recovery; or (2) Recycle to process;	Same as BPCTCA	Same as BPCTCA
Sodium Chloride (Solar Process)	Return of unused salts to the brine source	(1) Good housekeeping to prevent contamination of waste salts	Same as BPCTCA	Same as BPCTCA
Sodium Silicate	TSS 0.005	(1) Storage of wastes in an evaporation pond; or (2) Ponding and clarification	No discharge of pollutants in process waste water	Ponding or clarification and recycle of the treated waste water
Sulfuric Acid (Sulfur Burning Contact Process)	No discharge of pollutants in process waste water	(1) Acid containment and isolation with recycle to process or sale as weak acid;	Same as BPCTCA	Same as BPCTCA

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TABLE 3B. Summary of BPCTCA and BATEA (continued)

Chemical	BPCTCA		Best Practicable Control Technology Currently Available BPCTCA		BATEA		Best Available Technology Economically Achievable BATEA	
	Guideline				Guideline			
Lime	No discharge of pollutants in process waste water		(1) Dry Bag Collection System; or (2) Treatment of scrubber water by ponding and clarification and recycle		Same as BPCTCA		Same as BPCTCA	
Nitric Acid	No discharge of pollutants in process waste water		(1) Acid containment and isolation and reuse		Same as BPCTCA		Same as BPCTCA	
Potassium (Metal)	No discharge of pollutants in process waste water		(1) No process water used in manu- facture		Same as BPCTCA		Same as BPCTCA	
Potassium Dichromate	No discharge of pollutants in process waste water		(1) Replacement of barometric con- densers with non-contact heat exchangers; recycle of process liquor		Same as BPCTCA		Same as BPCTCA	
Potassium Sulfate	No discharge of pollutants in process waste water		(1) Evaporation of brine waters with recovery of magnesium chlorine; or (2) Reuse of brine solution in process in place of process water;		Same as BPCTCA		Same as BPCTCA	
	Flow liters/kg	Limitation kg/kg TSS Other			Flow liters/kg	Limitation kg/kg TSS		
Calcium Chloride (Brine Extraction)	330	0.0082 -	(1) Settling pond or clarification		No discharge of pollutants in process waste water	Same as BPCTCA plus (1) Replacement of barometric con- densers with noncontact heat ex- changers; and additional recycle		
Hydrogen Peroxide (Organic)	16,000	0.40 0.22 TOC	(1) Isolation and containment of process wastes; oil separation and clarification		No discharge of pollutants in process waste water	(1) Chemical decomposition for per- oxide removal (2) Carbon adsorption for organic removal		
Sodium (Metal)	9,000	0.23 -	(1) Settling pond; and (2) Partial recycle of brine waste solution after treatment		No discharge of pollutants in process waste water	100% brine recycle and reuse or sale of spent sulfuric acid		
Sodium Chloride (Solution Mining)	6,400	0.15 -	(1) Containment and isolation of spills, packaging wastes, scrubbers, etc; partial recycle to brine cavity		No discharge of pollutants in process waste water	Same as BPCTCA plus (1) Replacement of barometric con- densers with noncontact heat exchangers		
Sodium Sulfite	630	0.016 1.7** COD (As Cr <sub>2</sub> O <sub>7</sub> )	(1) Air oxidation of sodium sulfite wastes to sodium sulfate -- 94% effective; and final filtration to remove suspended solids		No discharge of pollutants in process waste water	Same as BPCTCA plus recovery of waste sodium sulfate		
Soda Ash (Sodium Carbonate) Solvay Process	6,900	0.17 -	(1) Settling ponds		6,900	0.10	(1) Settling ponds and clarification	

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TABLE 3B. Summary of BPCTCA and BATEA (continued)

Chemical	BPCTCA Guideline		Best Practicable Control Technology Currently Available BPCTCA		BATEA Guideline	Best Available Technology Economically Achievable BATEA
	Flow liters/kg	Limitation kg/kg	TSS	Other		
Hydrogen Peroxide (Electrolytic)	95	0.0025	0.002	CN <sup>-</sup>	(1) Ion exchange to convert sodium ferrocyanide to ammonium ferrocyanide which is then reacted with hypochlorite solution to oxidize it to cyanate solutions; and (2) Settling pond or filtration to remove catalyst and suspended solids	No discharge of pollutants in process waste water  (1) Same as BPCTCA plus segregation of waste water from cooling water and evaporation of the waste stream and recycle of the distillate
Sodium Dichromate and Sodium Sulfate	8,900	0.22	0.0005	Cr <sup>+6</sup> 0.0044 Cr (total)	(1) Isolation and containment of spills, leaks, and run off; and (2) Batchwise treatment to reduce hexavalent chromium to trivalent chromium with NaHS, plus precipitation with lime or caustic; and (3) Settling pond with controlled discharge	No discharge of pollutants in process waste water  Same as BPCTCA plus (1) Evaporation of the settling pond effluent with recycle of water and land disposal or recovery of solid waste
Chlor-alkali (Diaphragm Cell)	3,300	0.32	0.0025	Pb	(1) Asbestos and cell rebuild wastes are filtered or settled in ponds then land dumped; and (2) Chlorinated organic wastes are incinerated or land dumped; and (3) Purification muds from brine purification are turned to salt cavity or sent to evaporation pond/settling ponds; and (4) Weak Caustic—brine solution from the caustic filters is partially recycled	No discharge of pollutants in process waste water  Same as BPCTCA plus (1) Reuse or sell waste sulfuric acid (2) Catalytic treatment of the hypochlorite waste and reuse or recovery (3) Recycle of all weak brine solutions (4) Conversion to stable anodes
Chlor-alkali (Mercury Cell)	21,000	0.32	0.00014	Hg	(1) Cell rebuilding wastes are filtered or placed in settling pond, then used for landfill; and (2) Chlorinated organic wastes are incinerated or placed in containers and land dumped; and (3) Purification muds from brine purification are returned to brine cavity or sent to evaporation/settling ponds; and (4) Partial recycle of brine waste streams; and (5) Recovery and reuse of mercury effluent by curbing, insulation and collection of mercury containing streams, then treatment with sodium sulfide	No discharge of pollutants in process waste water  Same as BPCTCA plus (1) Reuse or recovery of waste sulfuric acid (2) Catalytic treatment of the hypochlorite waste and reuse or recovery (3) Recycle of all weak brine solutions

TABLE 3B. Summary of BPCTCA and BATEA (continued)

Chemical	BPCTCA			Best Practicable Control Technology Currently Available BPCTCA	BATEA		Best Available Technology Economically Achievable BATEA
	Guideline		Limitation kg/kg		Guideline		
	Flow liters/kg				TSS	Other	
Titanium Dioxide (Chloride Process)	90,500	2.2	Iron 0.36	(1) Neutralization with lime or caustic; and (2) Removal of suspended solids with settling ponds or clarifier-thickener; and (3) Recovery of by-products  e.g., V, Al, Si, Cr, Mn, Nb & Zr.	TSS 1.3	Iron 0.18	Same as BPCTCA plus additional clarification and polishing
Titanium Dioxide (Sulfate Process)	210,000	10.5	Iron 0.84	(1) Neutralization with lime or caustic; and (2) Removal of suspended solids with settling ponds or clarifier-thickener; and (3) Recovery of by-products	TSS 5.3	Iron 0.42	Same as BPCTCA plus additional clarification and polishing

\* Monthly average values. To convert from metric units to English units (lbs/ton), multiply the above values by 2.

\*\*COD of 2720 mg of dichromate ion per liter

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### Calcium Carbide

There is no process water involved in the production of calcium carbide. Ancillary water wastes such as cooling tower blowdowns and ion exchange regenerants are often present. There may also be water-borne wastes from air pollution control equipment.

Water-borne wastes from air-borne waste control equipment may be avoided by use of dry bag collector systems. Unlike aluminum chloride, the air-borne wastes from the calcium carbide process are all dusts -- coke and coal fines, limestone powder and calcium carbide from the packing station. Coke, coal and limestone fines, which constitute a significant fraction of the feed materials, may be profitably returned to the system. One plant uses only dry bag collectors and recycles the collected fines to the furnace.

Dry bag collection of air-borne fines eliminates waterborne wastes and makes it possible to reuse these fines. It also significantly reduces energy requirements by avoiding high energy drying costs needed for recovery of water wastes.

### Calcium Chloride

This chemical is obtained both from soda ash wastes and from natural salt deposits. The soda ash produces large amounts of calcium chloride as a by-product. Unreacted sodium chloride and other dissolved solids are present in this waste stream. After calcium chloride is extracted from this waste stream, the remaining calcium chloride, sodium chloride and other dissolved solids may be returned to the waste stream of soda ash manufacture. Extraction of calcium chloride from natural salt deposits is carried out in a major chemical complex and is scheduled within the next six months to be brought to virtually a zero process waste water pollutant discharge. Since both processes are dissimilar, there are no typical practices. The two major producers differ widely in their treatment approach.

From the soda ash process, recovery of calcium chloride is considered as a zero discharge process similar to sodium sulfate from the sodium dichromate process. There are no additional wastes generated as a result of this recovery.

The natural salt process, on the other hand, utilizes the integrated nature of the complex where it is produced to take advantage of every normal waste. Sodium chloride goes to chlor-alkali facilities. Magnesium chloride, which is often difficult to dispose, is isolated and used for other processes. Consequently this process for making calcium chloride also has no effluent in the particular complex where it is made. This is a good example of the previously discussed principle that wastes

from a complex should never be greater than the sum of the individual plants and usually will be significantly less.

### Calcium Oxide and Calcium Hydroxide

The process for producing calcium oxide involves no water-borne wastes. Waste water treatment is required only when wet scrubbers are used to remove entrained dust from the gaseous effluent.

Practices evidently vary from one plant to another as far as air pollution control practices are concerned. Some plants have no facilities for air-borne wastes, others use water scrubbers or dry bag collectors.

Water-borne wastes from air-borne waste control equipment may be avoided by use of dry bag collector systems. Unlike aluminum chloride, the air-borne wastes from the calcium oxide process are all dusts. This dust may be profitably returned to the system. The exemplary plant of this study uses only dry bag collectors and recycles collected fines.

Dry bag collection of air-borne fines not only eliminates water-borne wastes and makes it possible to reuse these fines, but it also significantly reduces energy requirements by avoiding high energy drying costs needed for recovery of water wastes.

If wet scrubbers are used, the scrubber solution may be discharged to a settling pond or vessel and recycled to the scrubbing system after sedimentation of suspended solids.

### Chlorine and Sodium or Potassium Hydroxide

Chlorine is produced by three major processes: mercury cells, diaphragm cells and Downs Cells. The other chemicals produced are sodium (Downs Cell only), sodium hydroxide and potassium hydroxide, variously. There is also quite often a direct burning hydrochloric acid plant in the complex.

The following chlorine discussion includes mercury and diaphragm cell productions. Downs Cell operation will be discussed under sodium, but the chlorine-based wastes are the same as for the mercury and diaphragm cells.

The chlor-alkali industry uses salt (sodium chloride or potassium chloride) as its raw material. Transformations of all sodium and chlorine chemicals can and have been made in chlor-alkali plants. There is a fortunate situation from the standpoint of waste reduction and zero discharge. In contrast, for example, are the soda ash process which produces large quantities of calcium chloride and the potassium dichromate process which produces large quantities of sodium chloride. Currently, there is only a

limited use for these waste products. Examples of how waste conversions can be made in the chlor-alkali process are given in the following equations:

- (1)  $2\text{NaCl} \longrightarrow 2\text{Na} + \text{Cl}_2$
- (2)  $2\text{Na} + 2\text{H}_2\text{O} \longrightarrow 2\text{NaOH} + \text{H}_2$
- (3)  $2\text{NaOH} + \text{Cl}_2 \longrightarrow \text{NaOCl} + \text{NaCl} + \text{H}_2\text{O}$
- (4)  $2\text{NaOCl} + \text{Cat.} \longrightarrow 2\text{NaCl} + \text{O}_2$
- (5)  $\text{Cl}_2 + \text{H}_2 \longrightarrow 2\text{HCl}$
- (6)  $\text{HCl} + \text{NaOH} \longrightarrow \text{NaCl} + \text{H}_2\text{O}$

Equations (1) and (2) show the product formations. Equation (3) represents tail gas scrubbing operations to remove chlorine gas from air effluents from the plants. Equation (4) shows conversion of sodium hypochlorite back to salt raw reactant materials. Equation (5) eliminates waste chlorine gas by direct burning of chlorine to produce hydrochloric acid. Equation (6) uses hydrochloric acid to neutralize waste sodium hydroxide, thereby producing salt for return to the system. Provided the water-borne waste streams are kept isolated from much larger cooling water streams, control and treatment techniques are entirely feasible.

Salt impurities have to be removed by precipitations before the brine solutions can be used in the cells. Treatment with soda ash, sodium hydroxide, and sometimes barium chloride, removes calcium, magnesium and sulfate ions as calcium carbonate, magnesium hydroxides and barium sulfates, respectively. The precipitated muds may be removed in ponds or clarification tanks. The muds may be disposed of by land dumping or fill.

Brine and sulfuric acid wastes may be neutralized with lime or sodium hydroxide, and ponded for reduction of suspended solids.

Water-borne mercury in the mercury cell process may be treated and removed by a variety of processes, usually employing precipitation of mercury sulfides, followed by mercury recovery by roasting or chemical treatment processes. Plants with typical recovery systems reduce mercury in the plant effluent to 0.11 to 0.22 kg/day (0.25-0.50 lb/day).

Total waste reduction depends on in-process control, isolation, treatment and reuse. There is no known problem which has not been solved by at least one plant of this survey.

Mercury cells are inherently "cleaner" processes than the diaphragm cells. Diaphragm cells have asbestos diaphragm deteriorations with suspended asbestos wastes. These have to be filtered out or allowed to settle in ponds. Sodium hydroxide produced in diaphragm cells has sodium chloride and other wastes and has to be purified for many uses.

A sodium sulfate purge, made by back-washing the precipitated salt slurry on the filter during the evaporation concentration of sodium hydroxide, is also needed to ensure satisfactory diaphragm cell operation. This sulfate purge can be handled by removing it from the system and using it elsewhere (as is done by exemplary diaphragm cell plant 057), by returning it for sulfate removal in the brine purification, or by recovery of sodium sulfate for sale.

Another waste from the diaphragm process, but not the mercury cell, is organic waste from the graphite anode. These are currently land disposed by the exemplary diaphragm cell plant, but are allowed to go out in waste streams at others.

Waste sulfuric acid from the chlorine-drying step may be used for neutralizations in other processes, sale, shipment to a regen sulfuric acid plant or concentration.

Collected chlorine gas for abatement of air-borne wastes can be burned to produce hydrochloric acid or converted to sodium chloride as discussed earlier.

Diaphragm cells are prone to develop cracks around their anode protective resin seals and lead salts from the underlying lead mountings can get into the effluents. Metal anodes can eliminate this problem and at a reported significant reduction in required cell electrical energy load.

The mercury cell, although "cleaner" than the diaphragm process, has a major waste problem in the form of mercury in the water-borne wastes. Major expenditures (discussed quantitatively in Section VIII) and in-process modifications have been made to alleviate this problem. Three plants discussed in section V reduce their mercury discharge to 0.00057, 0.000069 and 0.00007 kg/kg (0.0011, 0.000137, 0.00014 lb/ton). A small, 140 ton/day plant has reportedly reduced its mercury discharge to an average of 0.000143 kg/kg (0.000286 lb/ton). These low levels are accomplished by isolation of mercury-containing waste streams and chemical treatment of these streams.

Although no specific mention has been made of potassium hydroxide production, the same principles hold except that potassium is substituted for sodium.

By employing extensive treatment, control, recycle, and recovery, the chlor-alkali process may be operated with no discharge of process waste water pollutants to navigable waters.

#### Hydrochloric Acid

The only process considered in this study is chlorine burning. Only about ten percent of the U.S. production comes from this



process. Most hydrochloric acid is produced as a by-product of other processes. The chlorine-burning process is a simple one and capital equipment is relatively inexpensive. The process fits well with chlor-alkali complexes where low-cost or waste chlorine (and possibly hydrogen from mercury cells) is readily available.

There is no water-borne process waste during normal operation. A small amount of chlorine and hydrochloric acid wastes is developed during startup. Neutralization with sodium hydroxide can be followed by forwarding the neutralized stream to other chlor-alkali complex uses such as make-up water for brine solutions used in mercury or diaphragm cells. The size of the waste load, excluding that from the air-borne hydrogen chloride treatment, is small - 0.5 to 1.0 kg/kg.

Since there are no process wastes, spills, leaks, contributions from air-borne hydrogen chloride waste treatment equipment, and startup and upset wastes are the only concerns. Base treatment and control of these small miscellaneous wastes consists of neutralization with available sodium hydroxide followed by discharge to surface water.

Leaks, spills and startup wastes may be minimized by good housekeeping, operation, equipment maintenance and production planning. These wastes are not at this time directly related to a unit of production and may need to be limited on a case by case basis. To reduce water-borne wastes, containment and isolation techniques are required. Dikes, dip pans and other devices are used to control leaks and spills. Centralized collection and neutralization with sodium hydroxide can be followed by forwarding the neutralized stream to other chlor-alkali complex uses such as make-up water for brine solutions used in mercury or diaphragm cells. The size of the waste load, excluding that from the air-borne hydrogen chloride treatment, is small - 0.5 to one kg/kg.

#### Hydrofluoric Acid

Hydrofluoric acid sells for approximately \$550/kg. Therefore, the incentive for containment and recovery of leaks, spills and other product losses is understandably greater than for the other mineral acids. By the nature of the process, large quantities of cooling water are required. This is in the non-contact category, however, such that water-borne process waste loads are small.

Neutralization of sulfuric and hydrofluoric acid wastes with lime, followed by removal of precipitated calcium sulfate and calcium fluoride in settling ponds, reduces fluorides to 18 mg/l and calcium sulfate to approximately 2000 mg/l in treated water streams.

Segregation of the leaks, spills and sulfuric acid-containing wastes from the cooling water reduces the quantity of water which has to be treated. Also by in-process changes, such as using stoichiometric quantities of sulfuric acid in the process reactor, the sulfuric acid may be eliminated from the process waste water stream.

Lime treatment of the isolated wastes and settling pond removal of the precipitate reduces the fluoride content of this small stream to approximately 10 mg/l. This procedure gives waste with less than 0.5 kg total dissolved solids/kg (1 lb/ton) of hydrofluoric acid. This treatment makes closed cycle operation possible.

There are no air pollution problems for this process, but massive calcium sulfate solid wastes (3400-4250 kg/kg (6800-8500 lb/ton) of hydrofluoric acid) from the process reactor give both land disposal and rainwater runoff problems. Storage piles of this calcium sulfate should be located and contained so that materials such as calcium sulfate and residual lime or sulfuric acid are not conveyed by rainwater runoff to surface or underground fresh water streams.

#### Hydrogen Peroxide

##### a) Organic process

The organic process effluent generally contains waste hydrogen peroxide plus organic solvent used in the process. The nature of this solvent is considered a trade secret.

The hydrogen peroxide waste may be decomposed with scrap iron. The organic solvent may be removed by skimming the insoluble layer off the top of the water stream. The effluent may then be passed into a settling pond for removal of suspended solids or organic solvent interaction with suspended solids from other processes. Additional isolation, containment and treatment of wastes with scrap iron for peroxides and skimming separation for organics further reduces the waste loads.

Organics may be removed from this waste water stream by biological digestion or carbon adsorption treatment.

##### b) Electrolytic process

The electrolytic process for making hydrogen peroxide is represented by a single U.S. plant (100). Its effluent has practically the same composition as the incoming water, because the relatively very small amount of process water discharged is combined with the very large cooling water stream. Present levels were accomplished by in-process controls. The total water flow into the plant is about 41,600 cu m/day or 3,470,00 l/kg



(11,000,000 gal/day or 11,000,000 gal/ton). 75.7 cu m/day or 6300 l/kg (20,000 gal/day or 1830 gal/ton) is treated by ion exchange and used for boiler feed and process water. Discharges of this waste include 3.8 cu m/day or 316 l/kg (1000 gal/day or 92 gal/ton) of ion exchange blowdown, 26.5 cu m/day or 2200 l/kg (7000 gal/day or 640 gal/ton) of boiler blowdown and 1.1 cu m/day or 95 l/kg (290 gal/day or 27.6 gal/ton) of process water effluent. This latter stream may be eliminated by simple procedures such as total evaporation which is economically feasible because of the small quantity.

#### Nitric Acid

There are generally no water-borne process wastes. There are usually no water-borne wastes from air pollution abatement practices. Cooling water requirements are high. Minor water-borne wastes are due to leaks, spills and washdowns and ancillary systems such as cooling towers.

Provisions may be made for handling and neutralizing spills and leaks. Neutralization can be done with limestone, oyster or clam shells, lime or sodium hydroxide. Collected leaks, spills and washdowns may be returned to the process.

Diking of tanks, pump areas, loading and washing areas may be combined with isolation and reuse of leaks, spills and washdowns. Diking of large tanks should be sufficient for complete containment. Emergency ponds should be provided for major upsets. Limestone or seashell pond linings and ground coverings may be used for neutralizations.

#### Potassium Metal

There are no water-borne wastes from this process.

#### Potassium Chromates

Potassium dichromate is made from the reaction of sodium dichromate with potassium chloride. There is none of the massive ore waste present as in the sodium dichromate process. The only water-borne wastes from the major U.S. production facility emanate from contamination of once-through cooling water used in the barometric condensers. These are scheduled for replacement in 1974 by heat exchangers using non-contact cooling water. This will result in no discharge of waterborne wastes.

#### Potassium Sulfate

The exemplary plant for production of potassium sulfate is plant 118. It is a closed cycle plant where water recovery is accomplished by distillation of 1,500 cu m/day (400 gpd).

#### Sodium Bicarbonate

Typical treatment practices involve the settling of suspended solids in ponds before discharging the effluent to surface waters.

The untreated effluent from this process is essentially sodium carbonate in solution. In a complex, use for this solution may be made, probably at lower cost than for recovery. Present waterborne wastes are a relatively low 6.5 kg/kg (13 lb/ton) of product.

By keeping the waste stream small and the solids level high, evaporative techniques are feasible without undue expense. The evaporation process yields demineralized water for boilers, plus recovered product worth \$36/kg (\$32/ton). An alternative approach would involve total recycle.

#### Sodium Carbonate

The Solvay Process for making sodium carbonate (soda ash) is an old one dating back to the late 1800's. The Solvay plants are also old, the last U.S. plant being built in the 1930's.

The Solvay Process discharges more poundage of waste into surface water (solid basis) than any other chemical of this study (sodium chloride producers deep-well or store most of their effluent). The only redeeming feature is the relatively low toxicity of the waste.

Present treatment of water-borne wastes consists of removing most of the suspended calcium carbonate and other solids in unlined settling ponds followed by discharge to surface water. Adjustment for pH may or may not be done prior to this discharge.

The water-borne wastes from the Solvay Process are suspended and dissolved solids. The suspended solids are removed effectively by settling ponds and polish filtering can be done, if necessary, to reduce total suspended solids levels to 25 mg/l.

Dissolved solids are generally present in high concentrations. There are many treatment technologies available which can be used to eliminate the dissolved solids from the water effluent. However, most of them are not economically practical for the Solvay Process. Also, the geographical location of the plant has a major bearing on the treatment and disposal feasibility and costs.

A new plant of the Solvay Process is very unlikely to be considered. If a new Solvay Process plant were to be built, the process itself would likely be revised. Process modifications now in the laboratory or pilot plant stages would have to be

investigated and developed for commercial feasibility. The major area of revision would be in the recovery of ammonia from ammonium chloride. Use and recovery of magnesium hydroxide or decomposition of ammonium chloride to ammonia and chlorine are two such modifications that have been proposed. Recovery and reuse of the excess sodium chloride in the waste effluent could be accomplished by evaporation and crystallization techniques similar to those for the salt industry.

#### Sodium Chloride

Waste disposal is usually accomplished by pumping the brine wastes back into the well or mine when sodium chloride is made by the brine extraction process. In the solar evaporation process, brine wastes are normally returned to the source of the salt solution. Storage and recovery of magnesium and potassium salts is technically feasible, but appears uneconomical in most instances.

#### Sodium Dichromate and Sodium Sulfate

Typical treatment is to reduce the hexavalent chromium ion in the waste to trivalent chromium, remove the suspended solids in a settling pond, and discharge the clear solution to surface water. Ferrous chloride is often used as a reducing agent.

An exemplary chromium treatment and control plant (184) includes isolation of all chromium-containing, water-borne wastes from cooling water, collection of these wastes in tanks, batchwise treatment for hexavalent chromium reduction, and pond settling of suspended solids. The hexavalent chromium content remaining after treatment is very low. Provisions are made in this plant for collection and treatment of rainwater.

Although the treatment and control technologies described above are excellent for chromium treatment and control, two environmental problems remain -- disposal of large quantities of solids which gradually fill the settling ponds and discharge of large quantities of dissolved sodium chloride into surface water. The settled solids can be landfilled and the sodium chloride can be recovered by evaporation techniques and sold.

#### Sodium Metal

Sodium metal is produced in a Downs Cell Process. Chlorine, produced simultaneously with the sodium, is covered under chlorine. The treatment and control problems for chlorine, once it leaves the cell, are the same for the Downs Cell product as for the mercury and diaphragm cells.

The non-chlorine based wastes consist of brine purification muds, cell wastes such as bricks, graphite, sodium chloride and calcium

chloride, and sodium-calcium sludge from the sodium cooling and purification step. Settling ponds may be used for mud removal. Bricks, graphite and other solids may be landfilled. Sodium chloride and calcium chloride may be washed down and allowed to flow to surface water.

In the exemplary plant of this study, the only cell-based wastes not land dumped are the sodium and calcium chlorides. These salts, lost to the extent of an estimated 88 kilograms/kgg of sodium produced, result from cell dumpings, wash tanks, and run offs. These wastes are not currently controlled, and are allowed to run off over the land into surface water. Isolation and collection would make it possible to recover and reuse the sodium and calcium chlorides in the incoming brine system. One possible procedure would be to recycle this weak brine into the brine purification system. This stream can also be concentrated to recover, first any calcium sulfate or sodium sulfate, secondly sodium chloride, and finally, calcium chloride. Sodium chloride and calcium chloride can be dumped. Sodium sulfate can be sold or it may be containerized and disposed of.

Treatment methods for chlor-alkali facilities to eliminate the discharge of process waste water pollutants are applicable to chlorine production using the Downs Cell Process.

#### Sodium Silicate

Contaminated waste streams containing sodium hydroxide, sodium silicate and filter aids may be sent to settling ponds to remove suspended solids. Waste water may then be neutralized and discharged to surface water.

The wastes from sodium silicate plants are minor such that closed loop zero discharge operation is feasible.

#### Sodium Sulfite

The wastes from this process are primarily sodium sulfite and sodium sulfate. The sulfites constitute a heavy chemical oxygen demand (COD). Typical treatment, at least until recently, has consisted of using large quantities of cooling water to dilute the waste load.

Technology is now being applied to effect a ninety-five percent conversion of sulfite to sulfate by air oxidation.

Recovery of the sodium sulfate from the effluent eliminates process waste is technologically and economically feasible. Recovery eliminates the sulfite process waste and provides both a saleable product and a supply of high quality demineralized water for boiler, cooling tower, or process use.



## Sulfuric Acid

There are generally no process wastes from the sulfur-burning sulfuric acid plants. The only water-borne wastes result from spills, leaks, washdowns, and air-borne sulfur dioxide scrubbers.

Leaks, spills and washdowns may be detected by monitoring pH instrumentation. In-process leaks give serious corrosion problems so that shutdown and repair is in order as soon as these leaks are detected. Neutralization with lime or sodium hydroxide is used to control the pH level of the effluent.

Containment, isolation, and reuse or neutralization of minor leaks, spills and washdowns may be obtained with dikes, catch pans, sumps and drain systems. Major storage tanks should be sufficiently diked for complete storage tank capacity containment. Pond linings and pertinent plant grounds coverings of limestone or seashells can provide automatic neutralization. Pollution devices to remove sulfur dioxide sometimes contribute to the water-borne waste load. This may be avoided by utilizing sulfur dioxide removal processes which do not generate waste water streams. They should be used for all future installations. These non-water waste processes include double-absorption add-ons (for existing plants), and molecular sieve processes. Several other processes are either in commercial or developmental status.

Existing sulfur dioxide control equipment which involves water-borne waste can be converted to a waste-free basis by concentration and recovery of dissolved solids. A sulfuric acid plant in Finland neutralizes its scrubber effluent and concentrates the salt solution for use as fertilizer feed.

## Titanium Dioxide

The titanium dioxide industry is in a state of flux. Rutile is in a very short supply and most chloride process producers need this ore or a synthetic version of it. "Synthetic rutilites", or beneficiated low grade ores, are being offered by various foreign and a few domestic suppliers. A company in Japan has operated a 27,000 kkg (24.6 ton) plant since 1971 and is expanding to 40,000 kkg (36.4 tons). One U.S. company has announced a proposed 45,000 kkg/yr (41,000 ton/yr) plant using Australian technology. A comprehensive discussion of ore deposits, their composition, and beneficiation techniques may be found in Dr. Thomas S. Mackey's article "Alteration and Recovery of Ilmenite and Rutile", Australian Mining, November 1972, pp. 18-94.

### a) Chloride process

Waste streams for the chloride process fall into two categories:

1. Chlorination wastes composed of sludge from titanium tetrachloride losses and
2. Wastes incurred during the oxidation process and treatment of titanium dioxide product.

Base level treatment usually includes ponding to remove titanium dioxide, ore, coke and other settleable solids.

Three techniques for more effective treatment or disposal of chloride process wastes are available; neutralization of acids and conversion of metallic chlorides to insoluble oxides, ocean barging and deep welling.

A full chemical treatment system is used in plant 009. Chemical neutralization tanks, a clarifier, a thickener, and filters followed by a pond system are used for full acid neutralization, conversion and precipitation of metallic oxides, and concentration of suspended solids into a sludge. The sludge is disposed of as land fill. Both of the main chloride process waste streams, chlorination solids and oxidation process and titanium dioxide product-treatment wastes, are put through the chemical treatment system. The water-borne wastes from the system consist primarily of dissolved calcium chloride.

Deep-welling of the chlorinated wastes is practiced by plant 160. The oxidation and titanium dioxide product treatment wastes are sent through a settling pond system and discharged to surface water. Such deep well disposal is not a general solution to waste abatement practices, since it is not geologically feasible in many sections of the country. Ocean barging is also used to dispose of chloride process wastes, but this method of disposal is not universally applicable either. Both of these disposal techniques are subject to stringent permit requirements and must be consistent with local, State and Federal regulations.

The major chloride process wastes, particularly when low grade ore is used, are ferrous and ferric chlorides. Various proposals have been made for disposing of these chlorides. Included in these proposals are processes for decomposing the iron chlorides to iron oxide and hydrochloric acid (favored for pickle liquor recovery), a process for oxidation of iron chlorides to iron oxides and chlorine, and sale of the iron chlorides as such. Beneficiation of ore by chlorination, separation of iron chlorides, and dechlorination of the iron chlorides is another procedure. All of the above are still in the exploratory, laboratory, pilot plant or other preliminary stage at this time. Bureau of Mines research is already being carried out.

### b) Sulfate process

Approximately 2,000 kg of sulfuric acid and 1,000 kg of metallic sulfates/kg of product are discharged from the sulfate process.



Low grade ores used in the process contribute major quantities of metals which may someday be profitably extracted.

Waste streams generated by the sulfate process include:

- (1) sludge from the dissolving step and filtration,
- (2) copperas,
- (3) strong acid cuts,
- (4) weak acid cuts, and
- (5) titanium dioxide losses.

Wastes may be collected and sent to a settling pond for suspended solids removal.

Possible treatment and control technologies include filtration and disposal of the sludge from the dissolving step by land dumping, neutralization of both strong and weak acid cuts with limestone, followed by lime treatment to raise the pH to approximately 8 and precipitate iron and other metallic oxides and hydroxides. The conventional chemical treatment system of neutralization tanks, clarifiers, thickeners, filters or centrifuges and ponds may be employed for this purpose.

Ocean barging of the strong acid wastes, sludges and metallic sulfates is now used for disposal by some plants. Uncertainty about the future of this disposal method currently clouds its general application. Also, the weak acid and other wastes are still in many cases being discharged to surface water without significant treatment.

A pilot New Jersey Zinc Company with contract assistance from EPA is investigating the feasibility of acid recovery. Acid recovery is accompanied by treatment of the weak acid, metallic sulfates and titanium dioxide losses in the same type of chemical treatment system as discussed for complete neutralization. Acid recovery reduces the solid waste load inherent with complete neutralization and also decreases the amount of water-borne wastes. Costs are lower for this approach than for complete neutralization.

#### GENERAL METHODS FOR CONTROL AND TREATMENT PRACTICES IN THE INDUSTRY

Organic content and biological oxygen demands of the effluents for inorganic chemical plants are usually very low. Most alternative control and treatment technologies are well known, established and extensively practiced in the process of producing the inorganic chemicals of this study. Practices such as chemical treatment (neutralization, pH control, precipitation, and chemical reactions), filtration, centrifuging, ion exchange, demineralization, evaporation and drying are all standard unit operations for the industry. Process instrumentation, monitoring

and control for the chemical industry is outstanding. Another characteristic of the waste effluents from the inorganic chemical plants of this study is that they differ widely in both chemical nature and amount. Table 39 shows typical water-borne waste loads for the inorganic chemicals included in this study. Soda Ash (Solvay) and titanium dioxide (sulfate process) have raw waste loads in excess of the amounts of chemicals produced. On the other hand, chemicals, such as the mineral acids, calcium carbide and aluminum chloride, generate almost no water-borne wastes. Soda ash (Solvay) wastes are neutral salts while titanium dioxide (sulfate process) wastes are strongly acidic. Therefore, control and treatment technology has to be applied differently for each chemical.

Typical control and treatment technology in use on inorganic waterborne wastes today includes neutralization and pH control on effluent streams, ponds for settling of suspended solids, emergency holding, and storage, and discharge of the neutralized and clarified effluent to surface water.

Discharge of acidic or alkaline wastes to surface water is uncommon. Harmful wastes such as mercury, arsenic, cyanides, chromium and other metals are being removed with increasing efficiency. Technology has been developed for reduction of these harmful materials to very low levels.

Profitable waste segregations and recoveries, closed cycles, leak and spill containments, and in-process waste reductions are demonstrated in the industry. Some of these waste abatement programs have not involved much money, but most have been expensive. Numerous plants have reported program costs ranging from several thousand to several million dollars.

Waste abatement for the inorganic chemicals industry may be accomplished by a variety of methods. These methods may be divided into control and containment practices and treatment techniques. In many cases the control and containment practices are more important than subsequent treatments as far as feasibility and costs of waste treatment are concerned. The reasons for this are discussed in the following sections.

#### In-process controls

Control of the wastes includes in-process abatement measures, monitoring techniques, safety practices, housekeeping, containment provisions and segregation practices. Each of these categories is discussed including the interactions with treatment techniques.

TABLE 39. Typical Water-Borne Loads for Inorganic Chemicals of this Study

Chemical	Annual Production kkg	Waste Load*	Total Waste* kkg/yr
		kg/kkg Product	
Sodium Chloride	39,000,000	150	5,850,000
Soda Ash (Solvay)	3,630,000	1,500	5,440,000
Titanium Dioxide (Sulfate)	374,000	5,000	1,870,000
Chloride (Non-Rutile)	186,000	400	744,000
Chloride (Rutile)	64,000	75	4,800
Chlorine-Sodium Hydroxide	8,600,000	150	1,300,000
Sodium	150,000	150	22,500
Sulfuric Acid	27,200,000	0.5	13,600
(Sulfur Burning)			
Sodium Dichromate	136,000	58	13,600
Sodium Silicate	601,000	7.5	4,500
Aluminum Sulfate	1,020,000	3.5	3,570
Nitric Acid	6,300,000	0.25	1,590
Hydrogen Peroxide	64,000	20	1,270
Hydrofluoric Acid	281,000	4	1,120
Sodium Bicarbonate	186,000	4.5	840
Aluminum Chloride	31,000	24	725
Sodium Sulfite	209,000	3	625
Calcium Carbide	834,000	0.5	415
Hydrochloric Acid	200,000	0.5	100
(Direct Burning)			

NOTES:

- 1) Production figures were taken from Chem. & Eng. News, May 7, 1973, pp. 8-9 and "The Economics of Clean Water", Vol. III, Inorganic Chemicals Industry Profile, U.S. Dept. of the Interior, Federal Water Pollution Control Admin., March, 1970.
- 2) Typical waste loads were estimated from Final Technical Report, Contract No. 68-01-0020, Industrial Waste Study of Inorganic Chemicals, Alkalies and Chlorine, General Technologies Corp., July 23, 1971 (for EPA).
- 3) Titanium dioxide industry production figures were estimated from Chem. & Eng. News, February 19, 1973, pp. 8-9.

\*Solids basis.

Raw Materials

Purity of the raw materials used in the manufacturing process influences the waste load. Inert or unusable components coming into the process are generally discharged as waste.

Control of these impurities can be exercised in many instances. Ores can be washed, purified, separated, beneficiated or otherwise treated to reduce the waste coming into the process. An important facet of this approach is that this treatment can often be done at the mining site where such operations can be contained or handled on the premises. Reduction of shipping charges also favors beneficiation at the mine. Sometimes, as for "synthetic rutile" used in the titanium dioxide chloride process, beneficiated or high quality ore is necessary for developed process technology. Economics of raw material purity need to be balanced against the attendant waste treatment and disposal costs. As waste costs change, it may become more economical to use high quality materials.

Although pure raw materials reduce the inherent waste load, there are instances where, aside from economic factors, it may be desirable to use an impure material. In large manufacturing complexes, wastes from one process may be used for useful purpose in another. This procedure not only eliminates a bothersome waste from one process, it also gives economic value in the other. An example is the use of spent sulfuric acid in decom plants. Recycled raw materials serve the same desirable function.

Reactions

Except in rare cases such as the mining of salt or soda ash (trona), chemical reaction is involved in the manufacture of inorganic chemicals. Sometimes the reactants are stoichiometrically involved, but more often than not an excess of one or more of the reactants is used. The purposes of the excess vary but include:

1. certainty that the more expensive reactants are completely utilized;
2. yield improvement by driving the reaction in the desired direction;
3. safety concerns where it is imperative that a given reactant be eliminated;
4. shortening reaction time.

Excess reactants must be recovered for recycle or else they become part of the waste load. Often when the cost of the excess reactants was small, it had been more economical to let them go into the waste load rather than recover them. Sodium and calcium chlorides and sulfates are among the most common materials so handled.



Reactions may often be made to operate at more nearly stoichiometric conditions and thereby reduce waste loads. Also, the waste load may be deliberately changed in many cases by changing the reactant ratio. In the burning of hydrogen and chlorine to form hydrogen chloride, operating on the chlorine-rich side provides more troublesome waste than operating on the hydrogen-rich side. Similarly, aluminum chloride made on the chlorine-rich side requires air scrubbing to remove excess chlorine, while the aluminum-rich side does not.

Many chemical reactions are either faster and more complete at high temperatures or are exothermic and generate high temperatures. To produce, control and/or reduce these temperatures, cooling water and steam are often used. If the water or steam is used without contact (such as in a shell and tube heat exchanger), it is not contaminated. If, however, the water or steam contacts the reactants, then contamination of the water results and the waste load increases. Therefore, reaction heating and cooling should be non-contact whenever feasible.

#### Separations, purifications and recoveries

After reaction, the products, by-products, impurities, inerts and other materials present need to be separated, purified and recovered. Separations are carried out exploiting differences in boiling points, freezing points, solubility and reactivity to separate products from impurities, by-products and wastes. The efficiency of these determines:

1. the fraction of product that is lost as waste or has to be recycled;
2. the purity of the product;
3. control of air pollutants;
4. the recovery and/or disposition of by-products and wastes.

The more complete the separations into recovered product, raw materials that can be recycled, and wastes, the smaller the waste load from the process. The degree of separation actually achieved in the process depends on physical, chemical and economic considerations. These effects will be discussed for the individual chemicals of this study as they apply.

Cooling water and steam are also used in large quantities in the separation and purification steps. The same concepts apply as discussed in the reaction section. Indirect heating and cooling may, in many instances, virtually eliminate waterborne wastes.

#### Segregation

Probably the most important waste control technique, particularly for subsequent treatment feasibility and economics, is segregation.

Incoming pure water picks up contaminants from various uses and sources including:

1. non-contact cooling water
2. contact cooling water
3. process water
4. washings, leaks and spills
5. incoming water treatments
6. cooling tower blowdowns
7. boiler blowdowns

If wastes from these sources are segregated logically, their treatment and disposal may sometimes be eliminated entirely through use in other processes or recycle. In many instances, the treatment costs, complexity and energy requirements may be significantly reduced. Unfortunately, it is a common practice today to blend small, heavily contaminated streams into large non-contaminated streams such as cooling water effluents. Once this has been allowed to happen, treatment costs, energy requirements for these treatments, and the efficient use of water resources have all been comprised. In general, plant effluents can be segregated into:

1. Non-contaminated cooling water. Except for leaks, noncontact water has no waste pickup. It is usually high volume.
2. Process Water. Usually contaminated but often small volume.
3. Auxiliary Streams. Ion exchange regenerants, cooling tower blowdowns, boiler blowdowns, leaks, washings - low volume but often highly contaminated.

Although situations vary, the basic segregation principle is don't mix large uncontaminated cooling water streams with smaller contaminated process and auxiliary streams prior to full treatment and/or disposal. It is almost always easier and more economical to treat and dispose of the small volumes of waste effluents - capital costs, energy requirements, and operating costs are all lower. The use of segregation will be discussed for individual chemical processes.

#### Monitoring techniques

Since the chemical process industry is among the leaders in instrumentation practices and application of analytical techniques to process monitoring and control, there is rarely any problem in finding technology applicable to waste water analysis.

Acidity and alkalinity are detected by pH meters, often installed for continuous monitoring and control.

Dissolved solids concentrations may be estimated by conductivity measurements, suspended solids by turbidity, and specific ions by



wet chemistry and calorimetric measurements. Flow meters of numerous varieties are available for measuring flow rates.

The pH meter is the most universal of the in-line monitoring instruments. In acid plants, hydrochloric, sulfuric, phosphoric, nitric, hydrofluoric, and chromic acid leaks in coolers, distillation columns, pumps and other equipment can be picked up almost at once. Spills, washdowns and other contributions also become quickly evident. Alarms set off by sudden pH changes alert the operators and often lead to immediate plant shutdowns or switching effluent to emergency ponds for neutralization and disposal. Use of in-line pH meters will be given additional coverage in the control and treatment sections for specific chemicals.

For monitoring and control of harmful materials such as chromates, batch techniques may be used. Each batch is analyzed before dumping. This approach provides absolute control of all wastes passing through the system. Unless the process is unusually critical, dissolved solids are not monitored continuously. Chemical analyses on grab or composite effluent samples are commonly used to establish total dissolved solids, chlorides, sulfates and other low ion concentrations.

#### Safety, housekeeping containment

Many of the chemicals of this study or their wastes are either harmful and/or corrosive. Examples are the acids, chromates, chlorine, sodium hydroxide, sodium, and potassium. Mercury from chlor-alkali plants is an example of a harmful waste. Containment and disposal requirements may be divided into several categories:

1. minor product spills and leaks
2. major product spills and leaks
3. upsets and disposal failures
4. rain water runoff
5. pond failures

#### Minor spills and leaks

There are minor spills and leaks in all industrial inorganic chemical manufacturing operations. Pump seals leak, hoses drip, washdowns of equipment are necessary, pipes and equipment leak, valves drip, tank leaks occur, solids spill and so on. The quantity of waste water as a result of leaks and spills is usually reflected by the company or plant's managerial philosophy relative to housekeeping, washdown and production planning. Leaks and spills represent a potential hazard to workmen in the area of the spill or leak. In some cases the products are valuable (such as hydrofluoric acid and titanium dioxide where every pound lost is like throwing a quarter down the drain). In

other cases, where the financial loss may not be as great, personnel safety and equipment corrosion may become paramount. When a leak develops in the heat exchanger of a sulfuric acid plant, the plant shuts down before corrosion gets out of hand. Also, phosphorus is not handled carelessly.

Reduction techniques are mainly good housekeeping and attention to sound engineering and maintenance practices. Pump seals or type of pumps are changed. Valves are selected for minimizing drips. Pipe and equipment leaks are minimized by selection of corrosion-resistant materials.

Containment techniques include drip pans under pumps, valves, critical small tanks or equipment, and known leak and drip areas such as loading or unloading stations. Solids can be cleaned up or washed down. All of these minor leaks and spills should then go to a containment system, catch basin, sump pump or other area that collects and isolates all of them from other water systems. They should go from this system to suitable treatment facilities.

The above mentioned techniques are being used effectively in a number of plants today, and in many cases with enhanced profitability.

#### Upsets and disposal failures

In many processes there are short term upsets. These may occur during startup, shutdown or during normal operation. Although these upsets represent a very small portion of overall production, they nevertheless contribute to waste loads and must be treated. The upset products may be segregated and possibly reused. In the event that this can not be done, they must be disposed of. Disposal failures require emergency tanks and/or ponds or some other expediency for temporary holding or disposition.

#### Pond failures

Unlined ponds are the most common treatment facility used by the inorganic chemical industry. Failures of such ponds occur because they are unlined and because they are improperly constructed for containment in times of heavy rainfall.

Unlined ponds may give good effluent control if dug in impervious clay areas or poor control if in porous, sandy soil. The porous ponds will allow effluent to diffuse into the surrounding earth and water streams. This may or may not be detrimental to the area, but it is certainly poor waste control. Lined ponds are the only answer in these circumstances. Many ponds used today are large low-diked basins. In times of heavy rainfall, much of the pond content is released into either the surrounding countryside or, more likely, into the nearest body of water.

Again, whether this discharge is harmful or not depends on the effluent and the surrounding area, but it does represent poor effluent control and may not be permitted by local, State or Federal authorities.

Good effluent control may be gained by a number of methods, including:

1. Pond and diking should be designed to take any anticipated rainfall - smaller and deeper ponds should be used where feasible.
2. Control ponds should be constructed so that drainage from the surrounding area does not inundate the pond and overwhelm it.
3. Substitution of smaller volume (and surfaced) treatment tanks, coagulators or clarifiers can reduce rainfall influx and leakage problems.

#### Treatment and Disposal Methods

After the in-process control practices discussed in the previous section have been utilized, treatment is usually required for the contaminated streams. In general, these streams may be divided into one of three categories: cooling water, process water, and ancillary water.

Cooling water, either once-through or recycled by means of a cooling tower, should be relatively free of wastes. Any contaminants present would come from leaks (stream to be sent to emergency pond as soon as control monitoring picks it up) or recycle buildups (cooling tower) which are handled as ancillary water blowdowns. In either event, cooling waste contributions are small and treatment, except for incoming water purification, should not normally be needed.

Process and ancillary waterborne wastes do require treatment. The type, degree and costs involved will depend upon specific circumstances unique for each chemical. Various treatment techniques commonly used in the inorganic chemicals manufacturing industry include settling ponds or vessels, filtrations, chemical treatments, centrifugation, evaporation, drying, and carbon adsorption.

Incoming surface water from streams, lakes, or oceans is often filtered to remove suspended objects and solid particles, chemically treated for clarification (small suspended solids particle removal), controlled for pH and chlorinated for BOD control. Ion exchange is used to replace undesirable calcium, magnesium, carbonate and other ions which plate out on boiler, water tower and process equipment as they are concentrated, aerated or subjected to pH changes.

Waste water streams are often subjected to filtrations to remove minor suspended solids. Screens, cloths, cartridges, bags, candles and other mechanisms are used. The driving force may be gravity, pressure or vacuum. Usually the filters are precoated with diatomaceous earth or other filter aids.

Minor chemical treatments on waste water streams include neutralizations for pH control, equalization of streams in a pond or tank to minimize waste composition fluctuations, and chemical reactions or precipitations to remove undesired components.

Settling ponds or vessels are the major mechanism used for reducing the suspended solids content of water waste streams coming from the plant. Their performance and cost depends on the amount of waste involved and the settling characteristics of the solids suspended. In the lower cost category they are small, reflecting either fast settling and/or small, flow rates.

Costs for the above treatments may, in some cases, be derived in the following sections as extrapolations.

Higher cost treatments are rarely needed for incoming water (except in cases where either only very poor quality water is available or very low TDS is required). They are more applicable for treating waste effluents.

#### Ion Exchange and Demineralizations

Ion exchange and demineralizations are usually restricted in both practice and costs to total dissolved solids levels of 1000 to 4000 mg/l or less. Table 40 gives water compositions as a function of water treatments, including ion exchange and demineralization.

An ion exchanger may be simply defined as an insoluble solid electrolyte which undergoes exchange reactions with the ions in solution. An exchanger is composed of three components: an inert matrix, a polar group carrying a charge and an exchangeable ion carrying an opposite charge. The inert matrix today is usually a cross-linked polymeric resin containing the needed polar groups.

There are two types of ion exchangers: cation and anion. Cation exchangers contain a group such as sulfonic or carboxylic acid. These can react with salts to give products such as the following:

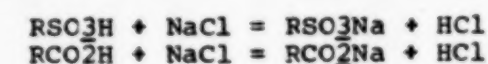




TABLE 40. Raw Water and Anticipated Analyses  
After Treatment

Substance	1	2	3	4	5	6	7	8	9
mg/l as Ca CO <sub>3</sub>									
<b>Cations</b>									
Calcium.....Ca++	100	35	58	1	1	-	-	100	100
Magnesium.....Mg++	100	58	7	1	-	-	-	100	100
Sodium.....Na++	100	100	85	298	164	-	-	100	100
Hydrogen Acidity.....H+	0	0	0	0	0	-	-	0	0
Total Cations.....	300	198	150	300	165	5	5	300	300
<b>Anions</b>									
Bicarbonate) HCO <sub>3</sub> -	150	0	0	150	15	-	-	150	150
Carbonate ) Alkalinity CO <sub>3</sub> -	0	35	21	0	0	-	-	0	0
Hydroxide ) OH-	0	0	0	0	0	-	-	0	0
Phosphate ) PO <sub>4</sub> -	0	0	0	0	0	-	-	0	0
<b>Anions</b>									
Chloride Cl-	75	79	64	75	75	-	-	75	75
Sulfate SO <sub>4</sub> -	75	79	63	75	75	-	-	75	75
Nitrate NO <sub>3</sub> -	0	0	0	0	0	-	-	0	0
Total Anions.....	300	193	150	300	165	5	5	300	300
Total Hardness.....	200	93	65	2	1	-	-	200	200
Alkalinity A (Methyl Orange).....	150	35	23	150	15	-	-	150	150
Alkalinity B (Phenolphthalein).....	0	17	14	0	0	-	-	0	0
Non-Carbonate Hardness.....	50	58	55	0	0	-	-	50	50
Sodium Alkalinity.....	0	0	0	150	164	-	-	0	0
<b>mg/l</b>									
Carbon dioxide.....as CO <sub>2</sub>	30	0	0	30	5-10	5-10	0	30a	30a
Silica.....as SiO <sub>2</sub>	15	A	5	15	15	15	0.02	15	15
Iron & Manganese.....as Mn & Fe	10	0.2b	0.2b	0.2	0.2	0.2	0.2	0.2c	0.3
Turbidity.....	50	0.2b	0.2b	0.2c	0.2c	0.2c	0.2c	0.2c	0.2c
Color.....	10	10	10	10	10	10	10	10	10
Total Solids (Cations + SiO <sub>2</sub> ).....	315	208	155	315	180	20	5	315	315

(continued on next page)

TABLE 40. Raw Water and Anticipated Analyses  
After Treatment (cont.)

1. Raw water
2. After cold lime softening and filtration
3. After hot process softening and filtration
4. Ion exchange softening
5. Sodium and hydrogen unit blend and degasification
6. Two-step demineralization (weak anion exchange) and degasification
7. Two-step demineralization (strong base anion resin) and degasification
8. Aeration and filtration
9. Manganese zeolite filters

- a. Some reduction will occur
- b. Filtered effluent
- c. With proper pretreatment
- d. Affected by pH adjustment
- e. Iron only

Note: Ion exchange processes assume that the water was adequately pretreated.



The above reactions are reversible and can be regenerated with acid.

Anion exchangers use a basic group such as the amino family.



This is also a reversible reaction and can be regenerated with alkalies. The combination of water treatment with both cation and anion exchangers removes the dissolved solids and is known as demineralization (or deionization). The quality of demineralized water is excellent. Table 41 gives the level of total dissolved solids that is achievable. Membrane and evaporation process water contain significantly higher solids content and need final polishing in a demineralizer if less than 3 mg/l dissolved solids level is required for the application. There are many combinations of ion exchangers which can be used for demineralizations.

Four types of demineralization units will be discussed in the cost analysis development to follow:

1. Fixed bed - strong cation - strong anion
2. Fixed bed - strong cation - weak anion
3. Mixed bed demineralizers
4. Special ion exchange systems.

Special ion exchange systems have been developed for concentrating high dissolved solids content (more than 1000 mg/l total dissolved solids), minimizing regenerant chemicals costs. Some of these special systems are listed in Table 42.

Ion exchange is rarely used to concentrate dissolved solids in waste streams unless some specific ion or ions need to be removed. In fact, usually little overall is gained by this technique since regenerations generate wastes that are often as troublesome to dispose of as the original dissolved materials. Also, the cost of treating waste water with a total dissolved solids concentration of only 1000 mg/l is not low. Demineralization can often be used for concentrating wastes.

#### Chemical Treatment

Chemical treatments for abatement of water-borne wastes are widespread. Included in this overall category are such important subdivisions as neutralization, pH control, precipitations and segregations, harmful and undesirable waste modification and miscellaneous chemical reactions.

#### a. Neutralization

Most of the inorganic chemicals of this study are either acidic, alkaline or react with water to give acidic or alkaline

TABLE 41. Water Quality Produced by Various Ion Exchange Systems

Exchanger Setup	Residual Silica mg/l	Residual Electro- lytes, mg/l	Specific Resistance ohm-cm @ 25°C
Strong-acid cation + weak-base anion	No silica removal	3	500,000
Strong-acid cation + weak-base anion + strong-base anion	0.01-0.1	3	100,000
Strong-acid cation + weak-base anion + strong-acid cation + strong-base anion	0.01-0.1	0.15-1.5	1,000,000
Mixed bed (strong-acid cation + strong-base anion)	0.01-0.1	0.5	1-2,000,000
Mixed bed + first or second setup above	0.05	0.1	3-12,000,000
Similar setup at immediately above + continuous re-circulation	0.01	0.05	18,000,000

TABLE 42. Special Ion Exchange Systems

System I

Application: Feedwater with high solids contents (above 1000 mg/l TDS). There are two variations of this system -- two-bed or threebed setup. Two-bed system consists of weak-base ( $\text{HCO}_3$ ) anion + weak-acid (H) cation exchangers followed by a decarbonator unit.  $\text{NH}_4\text{OH}$  and  $\text{CO}_2$  are used to regenerate the anion exchanger and sulfuric acid to regenerate the cation exchanger. In place of decarbonate a second weak-base (OH) anion exchanger is used in the three-bed Desal system.

System advantages: high flow rates; carbon dioxide recovery, good regenerant efficiency. Limitations: solids content of water must be less than 2000 mg/l; highly alkaline feedwater needed for best performance; iron in feedwater cannot be tolerated.

System II

Application: Feedwater with high solids content.

Also employs two- or three-bed setup. Two-bed system consists of strong-acid (H) cation + strong-base ( $\text{SO}_4$ ) anion exchangers followed by decarbonator. Sulfuric acid used to regenerate cation exchanger, raw water the anion exchanger. In three-bed system a weak-acid (H) cation exchanger precedes the strong-acid cation exchanger.

Advantages: raw water can be used to regenerate the strongbase anion exchanger; high quality rinse-water not required. Limitations: ratio of  $\text{SO}_4$  to Cl in feedwater must be high; requires high volume of rinse water; low capacity.

System III

Application: Feedwater with high solids content.

Four-bed systems consisting of: strong-base anion ( $\text{HCO}_3$ ) + weak-acid cation (H) + strong-acid cation (H) + weakbase anion (OH) exchangers.  $\text{NaHCO}_3$  is used to regenerate anion exchangers; sulfuric acid to regenerate cation exchangers.

TABLE 42. Special Ion Exchange Systems (continued)

System III (continued)

Application: (continued)

Advantages: may be used on feedwater containing up to 3000 mg/l solids, content; high capacity and regenerant efficiency. Limitations: number of columns required; low service flow rates; high cost of regenerants.

System IV

Application: Condensate desalination

Mixed-bed ion exchangers have been plagued by the fact that complete resin separation is difficult to achieve -- some cation resin remains mixed with anion resin after backwashing, with the result that sodium is released sooner (lower capacity); some leakage occurs (affecting water quality) since ammonia is usually present in condensate. This is overcome in Ammonex process by regenerating cation exchanger with acid and first regenerating anion exchanger with caustic and then with ammonia to remove the sodium present in anion exchanger.

System V

Application: Condensate desalination

Water quality and run length improved similarly as in Ammonex process except that anion exchanger is regenerated with caustic and lime rather than caustic and ammonia.

System VI

Application: Condensate desalination

Water quality and run length improved by separating mixedbed with strong caustic solution then regenerating beds in customary procedure; i.e., with acid for cation exchanger and caustic for anion exchanger.



solutions. Others have production wastes or byproducts of acidic or basic nature. Before disposal in surface water or other medium this acidity or alkalinity needs to be reduced and controlled. The most common method is to treat acidic streams with alkaline materials such as limestone, soda ash, sodium hydroxide, and lime. Alkaline streams are treated with acids such as sulfuric. Whenever possible, advantage is taken of the availability of acidic waste streams to neutralize basic waste streams and vice versa.

#### b. pH Control

The control of pH may be equivalent to neutralization if the pH is adjusted to approximately 7.0. As discussed in the earlier control section, control of excess acidity or alkalinity is best accomplished by pH meter monitoring. The usual acceptable range for pH control is 6.0-9.0 for discharge water.

#### c. Precipitations and Segregations

The reaction of two soluble chemicals to produce insoluble or precipitated products is the basis for removing many undesired waterborne (and airborne) wastes. The use of this technique varies from lime treatments to precipitate common sulfates, fluorides and carbonates, to sodium sulfide precipitations of mercury, copper, lead and other harmful metals.

#### d. Modifications

Chemical reactions can also be used to change or destroy undesirable wastes. Among the more common are the oxidation-reduction mechanisms. Cyanides can be oxidized to cyanates; hexavalent chromium reduced to the trivalent form; hypochlorites changed to chlorides; sulfites oxidized to sulfates. These examples and many others are basic to the modification of inorganic chemicals waterborne wastes to make them less troublesome.

#### Settling Ponds and Vessels

Many chemical treatments produce suspended solids which need to be removed from the waste streams. In the moving, agitated, often turbulent waste streams flowing through pipes, tanks, and channels, there is little opportunity to do this. In fact, it would usually be undesirable to do so in any event -- pipes and flow channels are not easy or economical to clean.

To facilitate settling of suspended solids, large quiet settling ponds and vessels are needed. Settling ponds are the foremost industrial treatment for removing suspended solids.

The size and number of settling ponds differ widely depending on the settling functions required. Waste streams with small suspended solids loads and fast settling characteristics require one or two small ponds with a surface area of less than 0.1-0.2 ha (0.25-0.5 ac). Other waste streams with heavier suspended solids loads and/or slower settling rates may require five to ten ponds and up to 405 ha (1000 ac) total surface area.

Although not as common as settling ponds, tanks and vessels are employed for reduction of suspended solids loads in inorganic chemical production waste streams. Commercially these units are listed as clarifiers or thickeners depending on whether they are light or heavy duty. They also have internal baffles, compartments, sweeps and other directing and segregating mechanisms to provide more efficient performance. This feature, plus the positive containment and control and reduced rainfall influence (smaller area compared to ponds), should lead to increasing use of vessels and tanks in the future.

#### Filtration (Major)

Major filtration equipment includes pressure and vacuum units of various designs, including plate-and-frame leaf and rotary constructions. Although it is entirely feasible for filtration equipment to be used for removing suspended solids from waste streams, most are not filtered. The preferred treatment for removing suspended solids is settling ponds. Filtrations are common for collection of solid wastes from harmful chemical treatments where complete removal is imperative. Sludges containing metal sulfides (mercury, arsenic, etc.) are good examples of materials handled in this way.

#### Centrifuging

When the force of gravity is not sufficient to separate solids and liquids to the desired degree, or in the desired time, more powerful centrifugal force can be utilized. Although there are many types of centrifuges, most industrial units can be broken down into two major categories -- solid bowl and perforated bowl. The solid bowl centrifuge, as its name indicates, consists of a rapidly rotating bowl into which the stream with suspended solids is introduced. Centrifugal action of the spinning bowl separates the solids from the liquid phase and the two are removed separately.

The perforated bowl centrifuge has holes in the bowl through which the filtrate escapes by centrifugal force. The solids are retained on the filter inside the bowl and removed either continuously (such as for the pusher types) or in batch fashion.



Centrifuges are not widely used for inorganic chemical waste streams, since it is rare that settling ponds or filters are not adequate for the same suspended solids removal job.

#### Carbon Adsorption

On the rare occasions that inorganic chemicals waste streams contain organic materials, one of the appropriate treatments to remove these organic components is carbon adsorption. When waste streams containing organic contaminants are passed through activated carbon beds, the organic material is adsorbed. When the carbon bed is saturated with this organic substance, the bed may be regenerated by burning off the adsorbed organic and returning the carbon to service.

#### Reverse Osmosis

The small pore size of the reverse osmosis membrane is both its strength and its weakness. Its strength comes from the molecular separations that it can achieve. However, it is susceptible to blinding, plugging, and chemical attack. Acidity, suspended solids, precipitations, coatings, dirt, organics and other substances can make it inoperative. Membrane life is critical and difficult to predict in many cases. Because of these restrictions its industrial applications are few. Fortunately, the inorganic chemistry industry water purification needs are similar to those of the areas where reverse osmosis has been shown to be applicable -- treatment of brackish water and low (500-20,000 mg/l) dissolved solids removal. Organics are usually absent, suspended solids are low or can be made low rather easily, acidity is easily adjusted, and most of the dissolved solids are similar to those in brackish water -- sodium chlorides, sulfates and their calcium counterparts.

The reverse osmosis membranes used commercially are generally one of two types -- flat sheet or hollow fiber. For maximum membrane area in the smallest space, various sheet configurations have been devised including tubes, spiral winding, and sandwich-type structures. Sheet membranes have been largely cellulose acetate, while hollow fibers have been largely polyamides. Costs for different membrane configurations are roughly comparable. The type selected depends upon the specific application.

Regardless of membrane type or material, the basic unit of construction is the module (or package of membrane materials). The module is usually integral and of the plug-in type, where a faulty module can be easily (but not inexpensively) replaced. The modules are the heart of the reverse osmosis process, with ancillary equipment such as pumps, tanks, piping, pretreatment facilities and other hardware performing peripheral functions. Module cost alone comprises one-third to one-half of the installed capital investment.

Detailed cost figures, both capital and operating, are given in Section VIII.

#### Evaporation Processes

Evaporation is the only method of general usefulness for the separation and recovery of dissolved solids in water. Other processes either involve mere concentration (reverse osmosis) or introduce contaminations for subsequent operations (demineralizer regenerants and chemical precipitations).

The evaporation process is well known and well established in the inorganic chemical industry. Separations, product purifications, solution concentrations are commonly accomplished by evaporative techniques. In-depth technology for handling the common dissolved solids in water waste streams has been developed in the soda ash, salt, calcium chloride, and sea water chemical industries. In addition, numerous desalination plants producing fresh water from brackish or sea water are scattered all over the world and have been in operation for a number of years. Seawater generally has approximately 35,000 mg/l dissolved solids (3.5 percent by weight) while brackish water has 2,000 to 25,000 mg/l depending on location.

Evaporation is a relatively expensive operation. To evaporate one kg of water, approximately 550 kg-calories of energy is required and the capital cost for the evaporating equipment is not low. For these reasons industrial use of evaporation in treating waste water has been minimal. As the cost of pure water has increased in portions of the United States and the world, however, it has become increasingly attractive to follow this approach.

The treatment of water waste streams by evaporation almost always has utilized the principle of multi-effects to reduce the amount of steam or energy required. Thus, the theoretical difficulty of carrying out the separation of a solute from its solvent is the minimum amount of work necessary to effect the particular change, that is the free energy change involved. A process can be made to operate with a real energy consumption not greatly exceeding this value. The greater the concentration of soluble salts, the greater is the free energy change for separation, but even for concentrated solutions the value is much lower than the 550 kg-cal/kg value to evaporate water. Multi-effect evaporators use the heat content of the evaporated vapor stream from each preceding stage to efficiently (at low temperature difference) evaporate more vapor at the succeeding stages. Thus the work available is used in a nearly reversible manner, and low energy requirement results. However, a large capital investment in heat transfer surface and pumps is required. The interaction of the capital equipment costs versus energy or operating costs will be discussed in detail in the treatment costs section.

### Drying

After evaporative techniques have concentrated the dissolved solids to high levels, the residual water content must usually be removed before recovery, sale or disposal. Water content will range from virtually zero up to 90 percent by weight. Gas- or oil-fired dryers, steam-heated drum dryers or other final moisture-removing equipment can be used for this purpose. Since this drying operation is a common one in the production of inorganic chemicals themselves, technology is well known and developed. Costs are mainly those for fuel or steam.

### Disposal Practices

Disposal of the waterborne wastes from inorganic chemicals manufacturing represents the final control exercised by the waste producer. A number of options are available. They include discharge to surface water -- river, lake, bay or ocean -- and where safe and permitted, land disposal by running the effluent out on land and letting it soak in or evaporate. Wastes may be disposed of into an industrial waste treatment plant. Treatment and reuse of the waste stream can also be practiced. In dry climates unlined evaporation ponds, if allowed, could be used.

Higher-cost disposal systems include lined evaporation ponds, deep well disposal, and high-cost treatment prior to disposal or recovery. Such methods are used for wastes which cannot be disposed of otherwise. These wastes contain strong acids or alkalis, harmful substances, or large quantities of dissolved solids.

Feasibility, use, and cost figures can be discussed for:

1. unlined evaporation ponds
2. lined evaporation ponds
3. deep wells

### Unlined Evaporation Ponds

Two requirements must be met for an unlined evaporation pond to be successfully utilized. First, it must be located in an area in which unlined ponds are allowed, and secondly, the rainfall in that area must not exceed the evaporation rate. This second requirement eliminates most of the heavily industrialized area. For the low rainfall areas, evaporation ponds are feasible with definite restrictions. Ponds must be large in area for surface exposure. Evaporation of large amounts of waste water requires large ponds. The availability and costs of sufficient land place another possible restriction on this approach.

### Lined Evaporation Ponds

The lined evaporation ponds now required in some sections of the country have the same characteristics as developed for the unlined ponds -- large acreage requirements and a favorable evaporation-rainfall balance. They are significantly higher in cost than an unlined pond. Such costs are developed in Section VIII. Reduction of the evaporation load is a significant advantage. For this reason, plus the short supply and high cost of water in much of southwestern United States, distillation and membrane processes are beginning to be used in these regions.

### Deep Wells

Deep well disposal can only be used under special conditions consistent with State and Federal regulations. While used for brine disposal in the petroleum and salt industries, deep wells are usually reserved for wastes such as strong acids, chromates, pickle liquor, and corrosive metallic salt solutions for which no other disposal system is available or environmentally acceptable. Deep well disposal should be considered only a temporary expedient until suitable recovery, reuse, or treatment methods are developed and demonstrated to be practical.

There are several reasons for this specialization, including:

1. Costs - A single well costs up to \$1,500,000 depending on depth, drilling ease and criticalness, casing, exploration and monitoring involved.

2. Geological - The geological structure in the area is of utmost importance. In many parts of the country, deep wells are not possible. Even in those sections where the geological structure permits their use, deep wells must be carefully planned and coordinated using the best geological information and expertise available.

3. Drilling Considerations - Deep wells are drilled by specialists using oil well technology. While this technology is well developed, there is always the possibility that something expensive will go wrong -- cracks, lost drills, impermeable formations, etc.

4. Reliability - Deep wells often plug or develop operating difficulties even after several years of good performance.

5. Extensive Pretreatment may be necessary to remove organics, suspended solids and other undesirable waste components.

6. The risk of contamination of underground potable water or seismic effects.

Most wells are approximately the same size and range in flow rate from 12.6-56.8 l/sec with the average being about 18.9-25.2 l/sec. This corresponds to approximately 1890 cu m/day capacity.



## SECTION VIII

### COST, ENERGY AND NON-WATER QUALITY ASPECTS CCST AND REDUCTION BENEFITS OF TREATMENT AND CONTROL TECHNOLOGIES

The inorganic chemical industry has large energy requirements for gas furnaces, kilns, calciners, electric furnaces, reactors, distillation columns, and evaporators and other common equipment. In contrast, treatment practices consume less than one tenth of one percent of this amount. Chemical reactions and pond settling, the most commonly used treatments, required almost no energy. Filtrations, centrifuging, and other separation techniques are still relatively low energy processes. The only two high energy treatments, evaporation and drying, are now rarely used. Utilizing these treatment techniques to the extent covered in the cost effectiveness discussions later in this section will still maintain treatment energy at a tiny fraction of the total energy for the industry. Table 43 summarizes cost and energy requirements for the manufacture of the inorganic chemicals of this report. To bring the processes to zero waterborne waste effluent through total recycle of process water, rough estimates for additional capital expenditures are 295 million dollars. Of this amount, three industries contribute almost eighty percent. These industries -- soda ash (Solvay Process), chlor-alkali, and titanium dioxide -- have vastly different situations from the other chemicals.

Titanium dioxide has no satisfactory replacement. It can absorb and pass on the large capital and operating costs needed for waterborne waste cleanup. This major clean-up is also long overdue. Development and application of existing treatment technology can save the titanium dioxide industry an estimated 100 million dollars over the full neutralization costs given in Table 43.

The chlor-alkali industry differs from both soda ash (Solvay) and titanium dioxide in that mainly in-process changes and more efficient use of raw materials are required to attain zero waterborne waste. There are many ways to accomplish this, some of which are suggested in Sections VII and VIII of this report.

Other industries that have major capital expenditures in Table 43, sulfuric acid, nitric acid, sodium metal (which is similar in process wastes to chlor-alkali plants), aluminum sulfate, sodium dichromate, and sodium chloride (brine or mining) have these costs primarily because of the large size of the industry or harmful wastes. Except for sodium chloride (brine or mining) and sodium dichromate, all waste abatement costs for these chemicals are below 1.5 percent of the list price.



TABLE 43. Summary of Cost and Energy Information for Attainment of Zero Discharge

Chemical	Additional Energy				Incremental Cost \$/ton	Percent of List Price	June, 1973	
	Additional Capital, \$	10 <sup>6</sup>		\$/metric ton			\$/ton	\$/metric ton
		Btu/yr	Kg cal/yr					
Aluminum Chloride	0	0	0	0	0	0	>255	280
Aluminum Sulfate	4,700,000	17,000	4300	0.90	1.0	1.4	62.80	69
Calcium Carbide	0	0	0	0	0	0	171.40	188
Hydrochloric Acid	250,000	0	0	0.05	0.06	0.04	110(100%)121	
Hydrofluoric Acid	1,180,000	3300	8350	13-16	14-18	2.5	560(100%)617	
Lime	0	0	0	0	0	0	19.50-	21.50-
							21.75	24
Nitric Acid	11,000,000	0	0	0.22	0.24	0.18	113(100%)124	
Potassium Metal	0	0	0	0	0	0	--	--
Potassium Chromates	90,000	210	53	4.65	5.15	0.97	480	528
Sodium Bicarbonate	0	0	0	0	0	0	88	97
Potassium Sulfate	1,570,000	680,000	162,000	1.60	1.16	3.7	42.50	47.50
Sodium Chloride (Solar)	0	0	0	2.20	2.42	25.9-11.0	8.50-20	9.40-22
Sodium Silicate	850,000	332,000	84,000	0.90	1.0	0.95	95	102
Sulfuric Acid	20,000,000	0	0	0.10	0.11	.33	28-32	30.75-35
Hydrogen Peroxide	350,000	0	0	1.00	1.10	0.2	460	505
(Organic)							(70%Sol'n)	
Sodium Metal	4,700,000	0	0	2.25	2.48	0.6	375	412
Sodium Sulfite	3,730,000	116,000	29,300	2.50	2.75	2.1	117	129
Calcium Chloride	1,040,000	0	0	0.20	0.22	0.5	42	46
Sodium Chloride (brine)	7,750,000	0	0	1.00	1.10	7.15-4.16	14-24	15.40-26.45
Chlor-Alkali	40,000,000	800,000	202,000	0.50	0.45	~0.5	Cl2\$75	\$83
				(combined product basis)			NaOH \$110	\$121
							(75%)	
Hydrogen Peroxide (Electrolytic)	15,000	870	220	0.25-.75	0.27-.83	0.1	460	507
							(70%Sol'n)	

(continued on next page)

TABLE 43. Summary of Cost and Energy Information for Attainment of Zero Discharge (continued)

Chemical	Additional Capital, \$		Additional Energy 10 <sup>6</sup>		Incremental Cost		Percent of List Price	June, 1973 List Price	
	Btu/yr	kg cal/yr	\$/ton	\$/metric ton	\$ /ton	\$/metric ton			
Sodium Dichromate	4,100,000	240,000	60,700	16	18	4.6	345	380	
Sodium Sulfate	0	0	0	0	0	0	24-33	26-36	
Soda Ash	*****25,000,000	200,000	50,200	1.60	1.76	4.5	35.50	39	
Titanium Dioxide (Chloride)	****74,000,000	675,000	170,000	64	70	11.4	550-570	605-615	
Titanium Dioxide (Sulfate)	96,000,000	555,000	135,000	96	103	17.1	550-570	605-615	
Totals	294,895,000	3,590,000	905,000	—	—	—	—	—	

\*Chemical Marketing Reporter, June 4, 1973.

\*\*Based on 3 million tons/year vacuum pan salt production from Salt, Bureau of Mines Minerals Yearbook, 1969.

\*\*\*Based on \$2.00/ton chlor-alkali production -- estimated from cost effectiveness data in Section VIII

\*\*\*\*Based on full neutralization plus demineralization costs as given in Section VIII

\*\*\*\*\*Based on deep-welling costs as in section VIII

For all chemicals except soda ash, titanium dioxide, sodium dichromate, and sodium chloride (solar), the yearly cost for total water-borne waste abatement is less than 4 percent of the current list price.

Energy requirements of  $9.05 \times 10^{11}$  kg cal/yr ( $3.6 \times 10^{12}$  BTU/yr) or the energy equivalent to burning 10,220 cu m (3.6 million gal) of fuel oil for the elimination of water-borne wastes for the chemicals of this study are less than that currently consumed by one large Solvay soda ash plant.

Thermal pollution was not encountered in this study nor was noise or other types of pollutions.

In general, plant size itself does not appear to be a significant factor influencing waste effluents on a kkg waste/kg of product basis. Multichemical complexes have an advantage over single isolated facilities on costs and options for waste utilization. Plant age does have some influence, with the new plants, naturally, being favored. These are by no means the controlling criteria, however. For example, nineteen exemplary plants used in the cost effectiveness development given later in this section have an average age of 21 years, with five plants of 30 years or greater age and six of 10 years or less age.

Geographical location is often a critical factor for waste disposal costs. Availability of deep welling, ocean barging, or solar evaporation options is an advantage. Also, the western United States has more incentive to recover and reuse ocean water than the east.

New plants being built can avoid major future waste abatement costs by inclusion of:

- (1) Dikes, emergency holding ponds, catch basins, and other containment facilities for leaks, spills and washdowns.
- (2) Piping, trenches, sewer, sumps and other isolation facilities to keep leaks, spills and process water separate from cooling and sanitary water.
- (3) Non-contact condensers for cooling water. Barometric condensers should be avoided.
- (4) A full water treatment system, including demineralization, reverse osmosis, evaporative and solids waste handling equipment when needed.
- (5) Efficient reuse, recycling and recovery of all possible raw materials and by-products regardless of inherent value. Sodium chloride and sodium sulfate are two by-products which frequently cause trouble.
- (6) Closed cycle water utilization whenever possible. Closed cycle operation eliminates all water-borne wastes. Generally, if water is pure enough for discharge, it is pure enough for reuse.

## Cost References and Rationales

Cost information contained in this report was obtained directly from industry during exemplary plant visits, from engineering firms and equipment suppliers, and from the literature. The information obtained from these latter three sources has been used to develop general capital, operating and overall costs for each treatment and control method. Costs have been put on a consistent industrial calculation basis of ten year straight line depreciation plus allowance for interest at six percent per year (pollution abatement tax-free money) and inclusion of allowance for insurance and taxes for an overall fixed cost amortization of fifteen percent per year. This generalized cost data plus the specific information obtained from plant visits was then used for the cost effectiveness estimates in this section and whenever else costs are mentioned in this report.

Cost developments, calculations, references and rationale for treatment and disposal techniques pertinent to the inorganic chemicals industry are detailed in Supplement A. In addition to the costs developed in Supplement A, costs for specific plant treatment systems are given in Supplement B. The combination of these two costs sources and engineering judgment extrapolations from them are used for cost effectiveness development.

## Definition of Levels of Control and Treatment

Using the general models as given in Figures 62 and 63, cost and energy effectiveness values for each chemical subcategory have been developed. Four levels of treatment and control are considered:

Level A -- Base level practices followed by most of the industry and exceeded by exemplary plants.

Level B -- Treatment and control practices at the average exemplary plant.

Level C -- Based upon the best technically and economically feasible treatment and control technology.

Level D -- Complete water-borne waste elimination. This level may or may not be economically feasible for the specific chemical.

## Aluminum Chloride

No water-borne process wastes are generated in the manufacture of aluminum chloride. The only ancillary waste stream results from wet air pollution control devices. Two exemplary plants have no wastes from this source. Plant 125 has been chosen for cost effectiveness development (see Table 44). This is a 30 year old

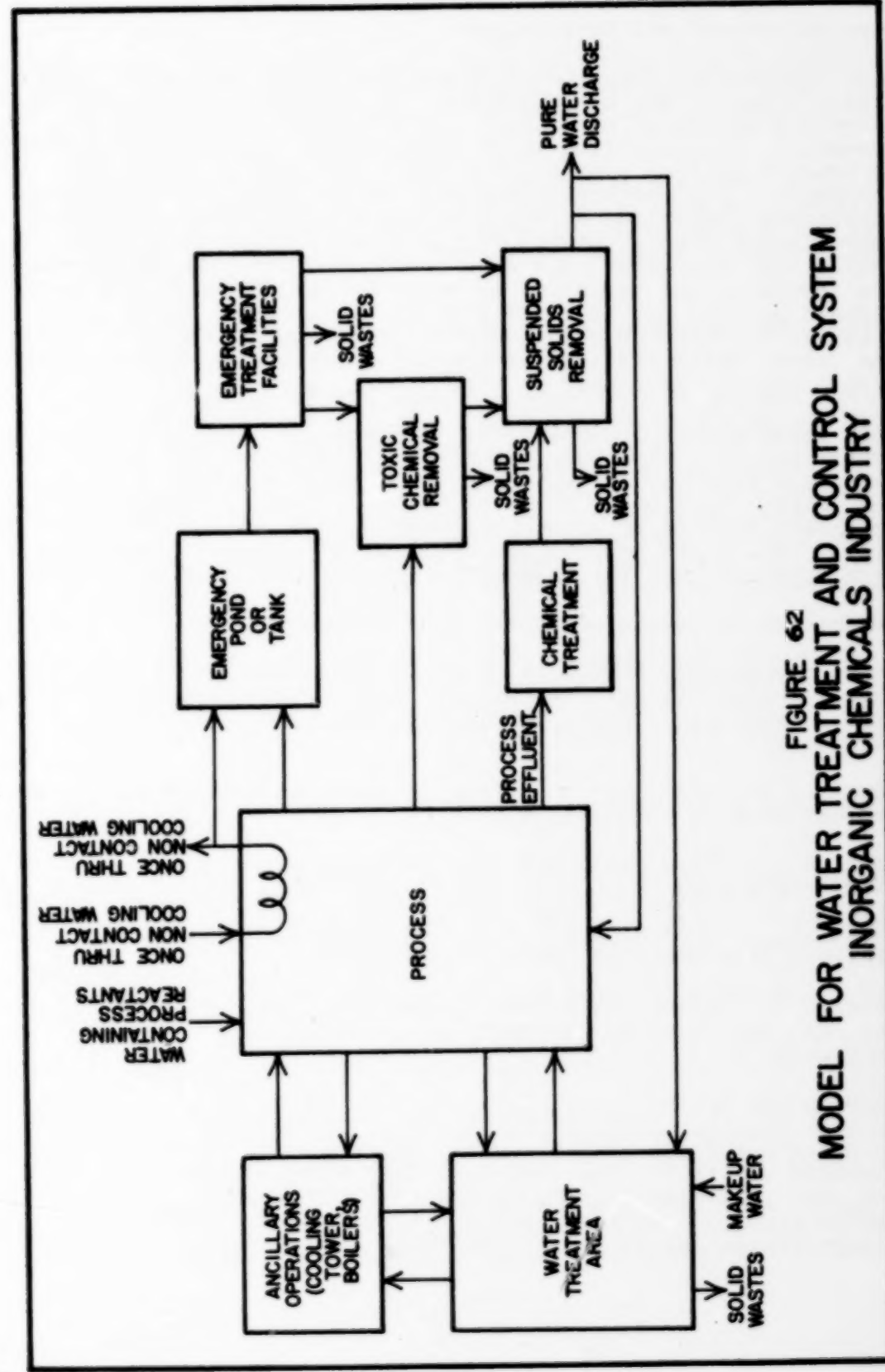


FIGURE 62  
MODEL FOR WATER TREATMENT AND CONTROL SYSTEM  
INORGANIC CHEMICALS INDUSTRY

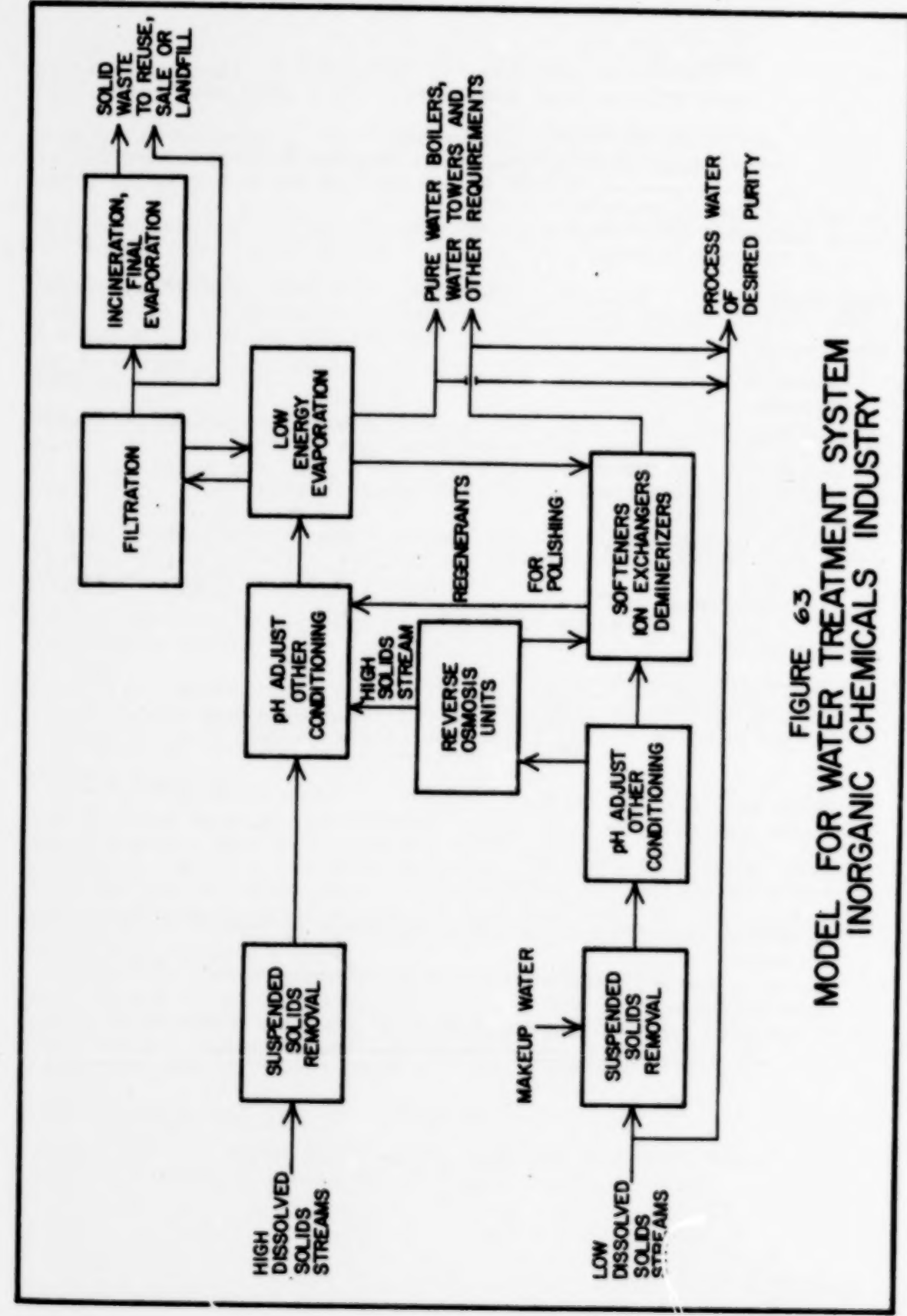


FIGURE 63  
MODEL FOR WATER TREATMENT SYSTEM  
INORGANIC CHEMICALS INDUSTRY



TABLE 44

## Water Effluent Treatment Costs

## Inorganic Chemicals

Chemical: Aluminum Chloride (22.5 kkg/day (25 tons/day) Capacity)

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B	C	D
Investment	25,000	100,000	100,000	100,000
Annual Costs:				
Interest + Taxes and Insurance	1250	5,000	5,000	5,000
Depreciation	2500	10,000	10,000	10,000
Operating and Maintenance Costs (excluding energy and power costs)	2000	0**	0**	0**
Energy and Power Costs	3500	~0	~0	~0
Total Annual Cost	9250	15,000***	15,000***	15,000***

## Effluent Quality:

Effluent Constituents Parameters (Units)	Raw Waste Load	Resulting Effluent Levels
(kg/kkg (lbs/ton))		
Aluminum Chloride + Chlorine (Airborne)	75(150)*	75(150)* -----2.5 (5)****-----
Level A - evaporation and reuse		
Level B - recycle of scrubber water		

\*Residual air-borne wastes (where scrubbers are used for air pollution abatement this is water-borne).

\*\*Operating costs of \$18,000/yr balanced by sale of product as aqueous aluminum chloride solution.

\*\*\*Credited to air pollution control water pollution control cost is zero.

\*\*\*\*Air-borne waste passing scrubber, scrubber liquor sold or recycled.

plant of nominal 22.5 kkg/day (25 ton/day) capacity. Treatment facilities have been recently installed.

Energy requirements are low (small pumps and stirrers) and are estimated to be 0.75 kwhr (1 hp-hr). Converting this to common units gives  $5.3 \times 10^6$  kg cal ( $2.1 \times 10^7$  BTU).

For the entire industry, the energy requirement would be  $1.7 \times 10^7$  kg cal ( $6.8 \times 10^7$  BTU).

Treatment costs for air pollution control are \$1.88/kkg (\$1.70/ton) of product. Treatment costs and energy requirements for water pollution control are zero.

## Aluminum Sulfate

Two exemplary closed-cycle plants, 049 and 063, were studied. Plant 063 is chosen for cost effectiveness analysis. This 46 year old plant has an average production of 36 kkg/day (40 tons/day). Cost effectiveness information is given in Table 45.

Energy requirements for pumps, clarifiers, drives, etc., are approximately 7.5 kwhr (10 hp-hr). Annual requirements are  $5.3 \times 10^7$  kg cal ( $2.10 \times 10^8$  BTU).

Entire industry energy for treatment is estimated as  $4.3 \times 10^8$  kg cal ( $1.7 \times 10^{10}$  BTU).

Costs for closed cycle zero effluent operation are \$1.87/ kkg (\$1.70/ton) of which \$1.00/kkg (\$0.90/ton) of product represents additional cost above typical operation in all plants.

## Calcium Carbide

The calcium carbide manufacturing process generates no water borne waste. The only possible contributions result from wet air pollution control devices used to remove dusts and particulates from the gas streams. Costs for treating air pollution abatement contributions to water effluents are credited to air pollution costs. Therefore, energy and costs for waste water treatment for calcium carbide are zero.

For information purposes, a cost-effectiveness sheet, Table 46, has been prepared showing air pollution abatement costs for plant 190. In this case air pollution control costs are zero since recovered raw materials pay for total annual costs.

## Calcium Oxide and Calcium Hydroxide

There is no water-borne waste from the process. Therefore, no cost or energy is involved.

TABLE 45.

## Water Effluent Treatment Costs

## Inorganic Chemicals

Chemical: Aluminum Sulfate (36 kkg/day (40 tons/day) Capacity)

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B	C	D
Investment	40,000	100,000		
Annual Costs:				
Interest + Taxes and Insurance	2,000	5,000		
Depreciation	4,000	10,000		
Operating and Maintenance Costs (excluding energy and power costs)	5,000	8,000		
Energy and Power Costs	--	1,000		
Total Annual Cost	11,000	24,000		
Effluent Quality:				
Effluent Constituents Parameters (Units) kg/kkg (lbs/ton)	Raw Waste Load	Resulting Effluent Levels		
Silicon Dioxide	20 (40)	1 (2)	-----0-----	
Titanium Dioxide	20 (40)	1 (2)	-----0-----	
Aluminum Oxide	10 (20)	1 (2)	-----0-----	
Aluminum Sulfate	0.25 (0.5)	0.05 (0.1)	-----0-----	

A -- Typical treatment taken as pond settling -- total pond area of 0.4 hectare (one acre) (unlined).

B -- Best average treatment level involves clarifiers plus additional ponds + level A ponds and closed cycle operation.

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TABLE 46.

## Water Effluent Treatment Costs

## Inorganic Chemicals

Chemical: Calcium Carbide (127 kkg/day (140 tons/day) Capacity)

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B	C	D
Investment	0	Not known		
Annual Costs:				
Interest + Taxes and Insurance		Not known		
Depreciation		Not known		
Operating and Maintenance Costs (excluding energy and power costs)	0	Not known		
Energy and Power Costs	0	Not known		
Total Annual Cost	0	0	0	0
Effluent Quality:				
Effluent Constituents Parameters (Units) Kg/kg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels		
Coke Dust	50(100)	50(100)	0	0
Furnace Dust	85(170)	85(170)	0	0
Packing Dust	10(20)	10(20)	0	0

Level A -- In many plants there are no dust collectors.

Level B -- Plant 190 installations are expected to pay for themselves in recovered raw material value. Therefore, annual air pollution control cost is zero.

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For informational purposes cost effectiveness Table 47 is given for eliminating air pollution. Cost is \$1.45/kg (\$1.32/ton) for dry bag collection installations. If water scrubbing plus elimination of water-borne wastes is more economical than \$1.45/kg (\$1.32/ton) of product, then water scrubbing and reuse may be used.

#### Calcium Chloride

Calcium chloride comes from two major sources, Solvay soda ash by-product and brine chemicals by-product. A 45 year old, 450 kkg/day (500 ton/day) brine reclamation plant, 185, is used for cost effectiveness development, as shown in Table 48.

Cost for elimination of present wastes is roughly estimated as \$0.22/kg (\$0.20/ton) of product.

No additional energy requirements are involved.

#### Chlorine and Potassium or Sodium Hydroxide

##### a) Mercury cell process

Both chlorine and sodium hydroxide are produced by the mercury cell process. Potassium hydroxide is produced similarly by starting with potassium chloride brine instead of sodium chloride.

Cost effectiveness values are developed in Table 49 using two year-old 158 kkg/day (175 ton/day) (chlorine basis) plant 098.

For zero water-borne wastes the cost above Levels A and B mercury removal is approximately \$1.00/kg (\$0.90/ton) of chlorine produced. Spreading these costs to chlorine and sodium hydroxide co-products reduces the value to approximately \$0.55/kg (\$0.50/ton) of products.

Roughly  $2.52 \times 10^9$  kg cal/yr ( $1.0 \times 10^{10}$  BTU/yr) additional energy is required for this plant.

Plants have now reduced water effluent mercury discharges to approximately 0.045-0.225 kg/day (0.1-0.5 lb/day) by spending Level A and B money. Some exemplary plants have spent Level C money (plant 098 is at this level).

##### b) Diaphragm cell process

Diaphragm cells also produce both chlorine and sodium hydroxide (or potassium hydroxide if potassium chloride brine is used).

Table 50 gives the progressive cost effectiveness development for one year old 2070 kkg/day (2300 ton/day) plant 057. Costs for

TABLE 47

#### Water Effluent Treatment Costs

#### Inorganic Chemicals

Chemical: Lime - Air Pollution Costs Only (281 kkg/day (310 tons/day) Capacity)

Treatment of Control Technologies Identified under Item III of the Scope of Work:				
	A	B	C	D
Investment	0	675,000	675,000	675,000
Annual Costs:				
Interest + Taxes and Insurance	0	33,750	33,750	33,750
Depreciation	0	67,500	67,500	67,500
Operating and Maintenance Costs (excluding energy and power costs)	0	35,000	35,000	35,000
Energy and Power Costs	0	2,500	2,500	2,500
Total Annual Cost	0	138,750	138,750	138,750
Effluent Quality:				
Effluent Constituents Parameters (Units) kg/kg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels		
Kiln Dusts	67(134)	67(134)	~0	~0

Level B -- Dry bag collectors installed.



TABLE 48.

## Water Effluent Treatment Costs

## Inorganic Chemicals

Chemical: Calcium Chloride (450 kkg/day (500 tons/day) Capacity)

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A*	B	C	D
Investment	0	200,000	200,000	200,000
Annual Costs:				
Interest + Taxes and Insurance	0	10,000	10,000	10,000
Depreciation	0	20,000	20,000	20,000
Operating and Maintenance Costs (excluding energy and power costs)	0	0	0	0
Energy and Power Costs	0	0	0	0
Total Annual Cost	0	30,000	30,000	30,000

## Effluent Quality:

Effluent Constituents Parameters (Units) kg/kkg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels			
Calcium Chloride	30(60)	30(60)	0.5(1)	~0	~0
Sodium Chloride	0.5(1)	0.5(1)	0	~0	~0
Ammonia	0.5(1)	0.5(1)	0	~0	~0

Level A -- Normally these wastes, as dissolved solids are discharged to surface water in non-exemplary of soda ash plants.

Level B -- Replacement of barometric condensers with non-contact heat exchangers.

Level C -- Elimination of packing station water-waste contributions.

\*Level A corresponds to present performance of "exemplary" plant in this table. Level B modelled to near future plans of this plant.

TABLE 49

## Water Effluent Treatment Costs

## Inorganic Chemicals

Chemical: Mercury Cell Chlor-Alkali (158 kkg/day (175 tons/day) Capacity)

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B	C	D
Investment	500,000	500,000	700,000	750,000
Annual Costs:				
Interest + Taxes and Insurance	25,000	25,000	35,000	37,500
Depreciation	50,000	50,000	70,000	75,000
Operating and Maintenance Costs (excluding energy and power costs)	55,000	55,000	61,000	64,000
Energy and Power Costs	1,000	1,000	2,000	7,000
Total Annual Cost	131,000	131,000	168,000	183,500

## Effluent Quality:

Effluent Constituents Parameters (Units) kg/kkg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels			
Sodium Chloride	50(100)	50(100)	50(100)	70(140)	~0
Sodium Hypochlorite	20(40)	20(40)	20(40)	~0	~0
Mercury	<0.05(0.1)	<1 x 10 <sup>-3</sup> (<2 x 10 <sup>-3</sup> )	<7 x 10 <sup>-5</sup> (<1.4 x 10 <sup>-4</sup> )	<7 x 10 <sup>-5</sup> (<1.4 x 10 <sup>-4</sup> )	~0

Level A -- Reduction of mercury to less than 1 x 10<sup>-3</sup> kg/kkg.

Level B -- Reduction of mercury to less than 7 x 10<sup>-5</sup> kg/kkg.

Level C -- Level B + catalytic conversion of sodium hypo chlorite to sodium chloride. Plant 098 is at this level.

Level D -- Level C + evaporation and reuse of sodium chloride. No effluent except cooling water from system. Drying sulfuric acid to other use or concentration.

TABLE 50.

Water Effluent Treatment Costs

Inorganic Chemicals

Chemical: Diaphragm Cell, Chlor-Alkali (1810 kkg/day (2000 ton/day) Capacity)

Treatment of Control Technologies Identified under Item III of the Scope of Work:

	A	B	C	D
Investment	45,000	65,000	495,000*	1,500,000
Annual Costs:				
Interest + Taxes and Insurance	2,250	3,250	3,250	75,000
Depreciation	4,500	6,500	6,500	150,000
Operating and Maintenance Costs (excluding energy and power costs)	24,000	224,000	224,000	224,000
Energy and Power Costs		1,000	1,000	1,000
Total Annual Cost	30,750	234,750	234,750	450,000

Effluent Quality:

Effluent Constituents Parameters (Units)	Raw Waste Load	Resulting Effluent Levels			
kg/kkg (Pounds/Ton)					
Calcium Carbonate sludge	12.25(24.5)	0	0	0	0
Sodium Hypochlorite	7.5(15)	7.5(15)	7.5(15)	0	0
Spent Sulfuric Acid	4(8)	4(8)	0	0	0
Chlorinated Hydrocarbons	0.7(1.4)	0.7(1.4)	0	0	0
Sodium Chloride	25.5(51)	25.5(51)	5(10)	5(10)	0
Sodium Hydroxide	22(44)	22(44)	4.5(9)	4.5(9)	0

Level A -- Settling Pond.

Level B -- Chlorinated hydrocarbons to disposal pit + sulfuric acid to sales, neutralization of sodium hydroxide and brine returned to system.

Level C -- Installation of chlorine burning hydrochloric acid plant for chlorine tail gas. Hydrochloric acid value equal to cost.

Level D -- Non-contact cooling substituted for barometric condensers - rough estimate.

\*Cost of installation -- 0 contribution to cost -- see Level C note.

attaining no discharge of process waste water pollutants are proximately \$0.55/kkg (\$0.50/ton) of product. For new facilities the cost would be considerably less, since non-contact condensers should be used in place of barometric condensers.

Additional energy requirements are negligible.

## Hydrochloric Acid

During normal operation the chlorine-burning hydrochloric acid manufacturing process has no water-borne wastes. Startup wastes are less than 0.5 kg/kkg (1.0 lb/ton) of product and are typically neutralized in sodium hydroxide solutions. Cost effectiveness information is given in Table 51 using plant 121 as a model. Addition of a small sodium hypochlorite destruction vessel plus a pump and transfer line for reuse in the chlor-alkali eliminates the process waste water discharge from the process. Total cost for zero effluent attainment is \$0.33/kkg (\$0.30/ton) of product, while the incremental cost for going from typical to zero effluent treatment levels is \$0.055/kkg (\$0.05/ton). Additional energy requirements are negligible.

## Hydrofluoric Acid

Hydrofluoric acid production, like that of the other mineral acids, generates a very low water-borne waste load. Good engineering, maintenance and housekeeping reduces the waste effluent to 0.5 kg/kkg (1.0 lb/ton) or less. A complete recycle zero discharge plant (152) of 27 kkg/day (30 ton/day) capacity and 15 years age, is chosen for cost effectiveness calculations as given in Table 48, column 4 (alternate B).

The large cost differential between Level C and Level B shows that two different approaches make a substantial difference in the costs involved. Plant 011 follows stoichiometric use of sulfuric acid, thereby eliminating \$30,000 neutralization chemical costs per year. It handles calcium sulfate and calcium fluoride dry by hauling to a land dump, thereby eliminating pond settling and dredging costs for another \$70,000/yr differential. In-process changes account, therefore, for a \$7.70/kkg (\$7/ton) difference in treatment costs.

Total cost to achieve no discharge of process waste water pollutants from plant 011 is \$17.60/kkg (\$16/ton) and for plant 152 is \$14.30/kkg (\$13/ton). The greatest portion of this cost is for handling and disposal of solid calcium sulfate, which has to be done in all plants.

Additional energy required for going from base level treatment to closed cycle operation is negligible. An additional 7.5 kw-hr (10 hp-hr) is allowed for pumping from collection ponds back to the system. This gives  $5.3 \times 10^7$  kg cal ( $2.10 \times 10^8$  BTU) or

TABLE 51:

## Water Effluent Treatment Costs

## Inorganic Chemicals

Chemical: Hydrochloric Acid (36 kkg/day (40 tons/day) Capacity)

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B*	C	D
Investment	10,000	10,000	15,000	15,000
Annual Costs:				
Interest + Taxes and Insurance	500	500	750	750
Depreciation	1,000	1,000	1,500	1,500
Operating and Maintenance Costs (excluding energy and power costs)	2,000	2,000	2,000	2,000
Energy and Power Costs	~0	~0	~0	~0
Total Annual Cost	3,500	3,500	4,250	4,250

## Effluent Quality:

Effluent Constituents Parameters (Units) kg/kg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels		
Chlorine & Hydrogen Chloride	0.5(1)	0.75(1.5)	0.75(1.5)*	0

Levels A and B -- Neutralization in sodium hydroxide solution followed by discharge to surface water.

Levels C and D -- Destruction of sodium hypochlorite in small pond or vessel and use of sodium chloride solution in chlor-alkali system. Chlorine-burning hypochloric acid units are always located in chlor-alkali complexes.

\*This corresponds to exemplary plant operation with wastes only during startup. Level I guideline recommendation modelled to C.

TABLE 52.

## Water Effluent Treatment Costs

## Inorganic Chemicals

Chemical: Hydrofluoric Acid (36 kkg/day (40 tons/day) Capacity)

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B*	C	Alternate B**
Investment	0	30,000	50,000	75,000
Annual Costs:				
Interest + Taxes and Insurance	0	1,500	2,500	3,750
Depreciation	0	3,000	5,000	7,500
Operating and Maintenance Costs (excluding energy and power costs)	50,000	52,000	60,000	165,000
Energy and Power Costs	~0	~0	1,000	5,000
Total Annual Cost	50,000	56,500	68,500	181,250

## Effluent Quality:

Effluent Constituents Parameters (Units) kg/kg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels			
Calcium Sulfate	3650(7300)	0	0	0	0
Sulfuric Acid	110(220)	0	0	0	0
Calcium Fluoride	62.5(125)	0.5(1)	0.25(0.5)	0	0
Hydrogen Fluoride	2.5(5)	2.5(5)	0.25(0.5)	0	0
Hydrofluorosilicic Acid	12.5(25)	12.5(25)	0	0	0
Silicon Dioxide	12.5(25)	12.5(25)	0	0	0

Level A -- Land dumping of calcium sulfate, minimizing acid by operating near stoichiometry requirements. Costs are all for trucking of calcium sulfate, calcium fluoride and contained sulfuric acid to land dump.

Level B -- Similar to Exemplary Plant 011 of this study.

Level C -- Closed loop extension of 011.

\*Exemplary plant operation, Level I guideline recommendation based on modelling to Level C, or equivalent to alternate Level B.

\*\*Exemplary closed loop plant 152 (27 kkg/day).



795/l/yr (210 gal/yr) of fuel oil. Total industry additional energy requirements are  $8.30 \times 10^6$  kg cal ( $3.3 \times 10^6$  BTU).

#### Hydrogen Peroxide

##### a) Organic process

The waste water effluent resulting from the manufacture of hydrogen peroxide by the organic process contains waste hydrogen peroxide plus an organic solvent. The nature of this solvent is regarded as a trade secret.

Cost effectiveness information is developed in Table 53 for exemplary plant 069, a twenty year old, 85 kkg/day (94 ton/day) facility.

Estimated additional cost to attain zero waste discharge is approximately \$1.10/kkg (\$1.00/ton) of hydrogen peroxide.

Additional energy requirements are negligible.

##### b) Electrolytic process

Hydrogen peroxide may be produced using an electrolytic process. Twenty year old plant 100 serves as the basis for the cost effectiveness information shown in Table 54.

Elimination of the process waste water discharge from this plant would cost approximately \$0.28 to \$0.83/kkg (\$0.25 to \$0.75/ton) of product produced.

Additional energy required would be  $2.2 \times 10^6$  kg cal ( $8.7 \times 10^6$  BTU).

#### Nitric Acid

There is no water-borne waste from the nitric acid manufacturing process, nor is there usually any contribution from air pollution treatment equipment. Only leaks, spills, monitoring and containment costs are involved.

For seven year old, 281 kkg/day (310 ton/day) plant 114, there are no effluent waste streams except boiler and cooling tower blowdowns. These are over 378,500 l/day (100,000 gal/day) in volume. Ancillary streams, however, are excluded from process waste water guidelines. Since no cost figures are available for nitric acid, they are estimated to be the same as those for sulfuric acid isolation and containment, \$160,000. Applying this cost to the 288 kkg/day (320 ton/day) plant gives \$0.24/kkg (\$0.22/ton) cost for isolation and containment of leaks and spills. No energy addition is involved.

TABLE 53'.

#### Water Effluent Treatment Costs

#### Inorganic Chemicals

Chemical: Hydrogen Peroxide (Organic Process) (85 kkg/day (94 tons/day) Capacity)

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B*	C	D
Investment	23,000	53,000	200,000	0
Annual Costs:				
Interest + Taxes and Insurance	1,150	2,650	10,000	10,000
Depreciation	2,300	5,300	20,000	20,000
Operating and Maintenance Costs (excluding energy and power costs)	3,000	3,000	5,000	5,000
Energy and Power Costs	~0	~0	~0	~0
Total Annual Cost	6,450	10,950	35,000	35,000

#### Effluent Quality:

Effluent Constituents Parameters (Units)	Raw Waste Load	Resulting Effluent Levels			
kg/kkg (Pounds/Ton)					
Organics	0.25(0.5)	0.1(0.2)	0.025(0.05)	0	0
Hydrogen Peroxide	20(40)	5(10)	5(10)	0	0

Level A -- Reduction of hydrogen peroxide with scrap iron, organics removal by mechanical separation.

Level B -- Level A + improved organics removal and spill containment.

Level C -- Closed loop process water, non-contact cooling water only effluent.

\*Not exemplary plant, modeled.

TABLE 54.

## Water Effluent Treatment Costs

## Inorganic Chemicals

Chemical: Hydrogen Peroxide - Electrolytic (12 kkg/day (13.2 ton/day) Capacity)

Treatment of Control Technologies Identified under Item III of the Scope of Work:

	A	B	C	D
Investment	-	12,500	15,000	
Annual Costs:				
Interest + Taxes and Insurance	-	625	750	
Depreciation	-	1,250	1,500	
Operating and Maintenance Costs (excluding energy and power costs)	-	1,600	2,000	
Energy and Power Costs	-	~0	1,000	
Total Annual Cost	-	3,475	5,250	

## Effluent Quality:

Effluent Constituents Parameters (Units)	Raw Waste Load	Resulting Effluent Levels		
kg/kkg (Pounds/Ton)				
Sodium Sulfate	0.75(1.5)	0.75(1.5)	0.75(1.5)	~0
Ammonium Sulfate	0.75(1.5)	0.75(1.5)	0.75(1.5)	~0

Level A -- There is no typical plant.

Level B -- Present plant operation

Level C -- Distillation to dryness 1136 liters/day (300 GPD)

## Potassium Metal

There are no process, air pollution or ancillary water wastes involved in the production of potassium metal.

## Potassium Chromates

Potassium dichromate is made from the reaction of sodium dichromate with potassium chloride. There is none of the massive ore waste present as in the sodium dichromate process. The only water-borne wastes from the exemplary 25 year old, 13.5 kkg/day (15 ton/day) plant 002 are from once-through cooling water used on the barometric condensers. Replacement of these condensers with non-contact heat exchangers, as planned for 1974, will eliminate the discharge of process waste water pollutants from this plant. Cost for this conversion is estimated at \$60,000. See Table 55.

The treatment differential in going from base Level A to zero discharge costs \$5.12/kkg (\$4.65/ton) of potassium dichromate.

Energy requirements for pumps, filters, centrifuges, and other equipment are taken as 7.5 kw-hr (10 hp-hr) or  $5.3 \times 10^7$  kg cal/yr ( $2.1 \times 10^8$  BTU/yr). Entire industry additional energy is estimated at the same value.

## Potassium Sulfate

The treatment and control cost effectiveness values for potassium sulfate based on plant 118 are developed in Table 56.

Costs for going from base treatment to zero effluent is \$2.38/kkg (\$2.16/ton) of potassium sulfate.

There is a relatively high energy recovery process with  $6.7 \times 10^{10}$  kg cal ( $2.65 \times 10^8$  BTU) or 1,000,000 l (265,000 gal) of fuel oil energy per year. For the entire industry the additional energy requirement is  $1.72 \times 10^{11}$  kg cal ( $6.8 \times 10^{11}$  BTU).

## Sodium Bicarbonate

Water-borne wastes from sodium bicarbonate facilities are small. Using plant 166 as a model, cost effectiveness values are developed in Table 57. Reducing the bicarbonate wastes to zero should be virtually cost free since current product losses should cover expenses.

There are no significant new energy requirements.

TABLE 55.

## Water Effluent Treatment Costs

## Inorganic Chemicals

Chemical: Potassium Chromate (13.5 kkg/day (15 tons/day) capacity)

Treatment of Control Technologies Identified under Item III of the Scope of Work:					
	A	B*	C	D	
Investment	20,000	50,000	110,000	110,000	
Annual Costs:					
Interest + Taxes and Insurance	1,000	2,500	5,500	5,500	
Depreciation	2,000	5,000	11,000	11,000	
Operating and Maintenance Costs (excluding energy and power costs)	0	10,000	10,000	10,000	
Energy and Power Costs	0	1,000	1,000	1,000	
Total Annual Cost	3,000	18,500	27,500	27,500	
Effluent Quality:					
Effluent Constituents Parameters (Units)	Raw Waste Load	Resulting Effluent Levels			
kg/kkg (Pounds/Ton)					
Sodium Chloride	400(800)	400(800)	0	0	0
Filter Aid	0.85(1.7)	~0.05(~0.1)	0	0	0
Potassium Dichromate	~0.5(~1)	~0.5(~1)	~0.5(~1)	~0	~0

Level A -- Discharge of all water to settling pond to remove filter aid.

Level B -- Centrifuge, filter, pumps, piping and installation for sodium chloride and filter aid removal. Salt value has been assumed zero.

Level C -- Non-contact heat exchangers installed.

\*Exemplary plant, Level I guidelines recommendations modelled to Level C, plans for 1974 for exemplary plant.

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TABLE 56.

## Water Effluent Treatment Costs

## Inorganic Chemicals

Chemical: Potassium Sulfate (454 kkg (500 tons) per day Capacity)

Treatment of Control Technologies Identified under Item III of the Scope of Work:					
	A	B	C	D	
Investment	40,000	700,000	700,000	700,000	
Annual Costs:					
Interest + Taxes and Insurance	2,000	35,000	35,000	35,000	
Depreciation	4,000	70,000	70,000	70,000	
Operating and Maintenance Costs (excluding energy and power costs)	10,000	124,000	124,000	124,000	
Energy and Power Costs	~0	166,000	166,000	166,000	
Total Annual Cost	16,000	395,000	395,000	395,000	
Effluent Quality:					
Effluent Constituents Parameters (Units)	Raw Waste Load	Resulting Effluent Levels			
kg/kkg (Pounds/Ton)					
Ore Muds	15(30)	0	0	0	0
Waste Liquor	2000(4000)	2000(4000)	0	0	0

Level A -- Pond settling of muds. Discharge of dissolved solids to surface water.

Level B -- Evaporation to recover liquor chemicals and water + Level A value of recovered chemicals not deducted from costs. Water value is also not deducted.

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TABLE 57.

## Water Effluent Treatment Costs

## Inorganic Chemicals

Chemical: Sodium Bicarbonate (272 kkg/day (300 ton/day) Capacity)

Treatment of Control Technologies Identified under Item III of the Scope of Work:

	A	B	C	D
Investment	10,000	15,000	15,000	15,000
Annual Costs:				
Interest + Taxes and Insurance	500	750	750	750
Depreciation	1,000	1,500	1,500	1,500
Operating and Maintenance Costs (excluding energy and power costs)	1,000	2,000	2,000	2,000
Energy and Power Costs	~0	~0	~0	~0
Total Annual Cost	2,500	4,250	4,250	4,250

## Effluent Quality:

Effluent Constituents Parameters (Units) kg/kkg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels			
Sodium Carbonate	30(76)	38(76)	38(76)	0	0
Sodium Bicarbonate	10(20)	10(20)	0	0	0
Rubbish	<2.5(<5)	0	0	0	0

Level A -- Settling pond, landfill for rubbish, discharge to surface water.

Level B -- Redissolve broken bags and waste sodium bicarbonate + Level A.

Level C -- Recycle sodium carbonate to Solvay Process system. Value obtained equal cost.

\*Exemplary plant plans to go to Level C in near future, hence Level I guidelines recommendations were modelled to Level C.

## Sodium Carbonate

The Solvay process produces approximately 1370 kg (3000 lb) of dissolved solid wastes for every kkg (ton) of product. These solids consist of slightly over 0.91 kkg (1.0 ton) of calcium chloride, which has high solubility, is difficult to obtain in anhydrous form, and spontaneously picks up moisture from the air when land dumped, and about 0.45 kkg (0.5 ton) of unreacted sodium chloride, also highly soluble.

Although there is a market for calcium chloride, this market can be supplied with 10 to 15 percent of the calcium chloride available from Solvay plants alone. Therefore, most of the available calcium chloride must be disposed of at zero value or less (disposal costs). The sodium chloride can be reused if it can be separated from the calcium chloride and other wastes, but the value of this raw material is low and recovery is uneconomical. Therefore, half a dozen Solvay plants discharge more waste to surface water than any other chemical subcategory and there is no general economically feasible treatment scheme to eliminate the discharge of these wastes. Costs are given below for Solvay process plant 166. This 2520 kkg/day (2800 ton/day), over 75 year old facility, is used for cost developments.

Treatment and Control Method	Capital Costs \$	Annual Cost \$
1. Coproduction of ammonium chloride with soda ash	34,000,000	26,000,000
2. Ammonia and hydrogen chloride from ammonium chloride	133,000,000	45,000,000
3. Ammonia and chlorine from ammonium chloride	80,000,000	34,000,000
4. Deep well disposal	6,000,000	1,600,000
5. Total evaporation plus ocean barging of solid wastes	51,000,000	31,000,000

Options 1, 2, and 3 are process changes or additions with high capital investments. The quantities of ammonium chloride, hydrogen chloride and chlorine produced either exceed the current demand or would be such major contributors that the market structure would be drastically altered. The other two options are disposal methods.

The only economically feasible disposal options for Solvay process soda ash wastes today are partial recovery of calcium chloride for sales or deep welling. Since the Solvay soda ash wastes are similar to those for brine salts and oil well salts, which are extensively deep-welled, a good case can be made for such disposal, if geologically feasible at the plant location (or close by). However, deep-well disposal may be practiced only under strictly regulated conditions, consistent with State and Federal laws.

Cost effectiveness values are developed using these two technologies in Table 58.

Additional costs for zero discharge of wastes to surface water are approximately \$0.55/kg (\$0.50/ton) of product. For deep-welling disposal alone, costs for zero waste effluent are \$1.76/kg (\$1.60/ton) produced. Additional energy requirements, primarily for calcium chloride recovery, are high. Estimated requirements for plant 166 are  $3.15 \times 10^{10}$  kg cal/yr ( $1.25 \times 10^{12}$  BTU/yr) or for the entire industry  $1.26 \times 10^{12}$  kg cal/yr ( $5.0 \times 10^{12}$  BTU/yr). Without calcium chloride recovery, about  $1.25 \times 10^{10}$  kg cal/yr ( $5.0 \times 10^{12}$  BTU/yr) for plant 166 or  $5.0 \times 10^{10}$  kg cal/yr ( $2.0 \times 10^{12}$  BTU/yr) for the industry, would be needed for deep welling.

Sodium Chloride

#### a) Solar evaporation process

It has been recommended that concentrated magnesium-rich residual brines or bitterns from solar salt manufacture be stored and eventually recovered for their chemical value. Taking Plant 059 as a model, cost effectiveness values are developed in Table 59.

One 146 ha (360 ac) pond is needed each year. While this storage capacity is available for the next five to ten years, obviously it cannot go on indefinitely. Use of these valuable mineral deposits should be made in the near future. Storage costs for solar salt bitterns for Plant 059 are \$2.42/kg (\$2.20/ton) of product.

Additional energy requirements are negligible.

#### b) Solution brine-mining process

Unlike the solar salt industry where all wastes are stored or disposed of in surface ponds, salt producers using the brine-mining process get their salt from underground deposits and return most wastes to the mine deposit.

Exemplary plant 030, a 49 year old, 1,000 kkg/day (1,100 ton/day) facility is used for cost effectiveness developments in Table 60. Complete elimination of process wastes in the plant effluent would cost, for a new plant, approximately \$0.28/kg (\$0.25/ton) of product. This assumes plant 030 technology plus initial installation of non-contact final condensers. Conveying and packing losses may be recovered dry and either reused or land (or well) disposed.

Elimination of all but 1 kg/kg (2 lb/ton) waste from plant 030 would cost approximately \$0.55/kg (\$0.50/ton) of product.

TABLE 58.

Water Effluent Treatment Costs

Inorganic Chemicals

Chemical: Soda Ash (2520 kkg/day (2800 tons/day) Capacity)

Treatment of Control Technologies Identified under Item III of the Scope of Work:					
	A	B	C	D	
Investment	500,000	21,500,000	27,500,000	27,500,000	
Annual Costs:					
Interest + Taxes and Insurance	25,000	1,075,000	1,375,000	1,375,000	
Depreciation	50,000	2,150,000	2,750,000	2,750,000	
Operating and Maintenance Costs (excluding energy and power costs)	375,000	3,175,000	3,675,000	3,675,000	
Energy and Power Costs	-	800,000	1,000,000	1,000,000	
Total Annual Cost	450,000	(1,080,000)	520,000	520,000	
<u>Profit</u>					
Effluent Quality:					
Effluent Constituents Parameters (Units) kg/kg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels			
Calcium Chloride	1100(2200)	1100(2200)	900(1800)	0*	0*
Sodium Chloride	500(1000)	500(1000)	500(1000)	0*	0*
Calcium Carbonate	85(170)	~0	~0	0*	0*
Calcium Oxide	135(270)	25(50)	25(50)	0*	0*
Calcium Sulfate	31(62)	2.5(5)	2.5(5)	0*	0*
Ash and cinders	40(80)	~0	~0	0*	0*
Silicon Dioxide	585(117)	~0	~0	0*	0*

Level A -- Settling ponds

Level B -- Level A + evaporation of 20% of stream to recover calcium chloride for sale at \$44/kg (\$40/ton) -- 8,280,000 value.

Level C -- Level B + deep well disposal.

\*No surface water effluent.

TABLE 59 .

Water Effluent Treatment Costs

Inorganic Chemicals

Chemical: Solar Salt (2540 kkg/day (2800 tons/day) Capacity)

Treatment of Control Technologies Identified under Item III of the Scope of Work:				
	A	B	C	D
Investment	14,400,000	14,400,000	14,400,000	14,400,000
Annual Costs:				
Interest + Taxes and Insurance	720,000	720,000	720,000	720,000
Depreciation	1,440,000	1,440,000	1,440,000	1,440,000
Operating and Maintenance Costs (excluding energy and power costs)	~0	~0	~0	~0
Energy and Power Costs	~0	~0	~0	~0
Total Annual Cost	2,160,000	2,160,000	2,160,000	2,160,000
Effluent Quality:				
Effluent Constituents Parameters (Units) kg/kg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels		
Bitterns	70,000(140,000)	0	0	0

Level A -- 1 new 360 acre unlined pond per year is needed. Costs are taken from Section VIII for unlined ponds.

TABLE 60 .

Water Effluent Treatment Costs

Inorganic Chemicals

Chemical: Sodium Chloride (Brine/Mining) (1000 kkg/day (1100 ton/day) Capacity)

Treatment of Control Technologies Identified under Item III of the Scope of Work:				
	A	B	C	D
Investment	-	500,000	1,000,000	600,000
Annual Costs:				
Interest + Taxes and Insurance	-	25,000	50,000	30,000
Depreciation	-	50,000	100,000	60,000
Operating and Maintenance Costs (excluding energy and power costs)	-	10,000	10,000	10,000
Energy and Power Costs	-	~0	~0	~0
Total Annual Cost	-	85,000	160,000	100,000
Effluent Quality:				
Effluent Constituents Parameters (Units) kg/kg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels		
Sodium Chlorine	50(100)	-	6(12)	1(2)
Brine Sludge	2.5(5)	-	0	0

Level A -- No information.

Level B -- Plant 030 technology, sludge returned to wells. Control system developed including \$425,000 damming, curbing, collection and pumping to wells, and \$63,000 instrumentation and miscellaneous pumps and piping.

Level C -- Level B + non-contact heat exchangers for barometric condensers.

Level D -- For new plants. Elimination of conveying and packing station losses peculiar to Plant 030.



Negligible additional energy would be required.

#### Sodium Dichromate

The sodium dichromate manufacturing process produces a waste stream containing high concentrations of suspended and dissolved solids primarily because of the chromium treatment process used. Two year old 149 kkg/day (164 ton/day) plant 184 is used as the model for cost effectiveness development as shown in Table 61.

Additional cost above typical treatment is \$17.60/kkg (\$16/ton) of product, of which \$13.20/ (\$12/ton) is already being spent in exemplary plant 184. Evaporation to recover dissolved salts costs \$4.40/kkg (\$4/ton) of product. Selling price of sodium dichromate is \$380/kkg (\$345/ton).

These figures illustrate the high cost of isolating, containing, treating and disposing harmful wastes. They also show that if the effluent streams can be kept small, 1,317 cu m/day (348,000 gal/day) in this case, removal of dissolved salts by evaporation is expensive, but not prohibitively so.

It is believed that, while the isolation, containment and treatment facilities of exemplary plant 184 are exceptional, there are more economical ways of achieving the same degree of chromium reduction.

Additional energy requirements are estimated to be  $2.5 \times 10^{10}$  kg cal ( $1.0 \times 10^9$  BTU) per year for plant 184. For the industry, using similar treatment (which is doubtful) to eliminate the discharge of process waste water pollutants, the additional yearly energy requirements would be  $6.05 \times 10^{10}$  kg cal ( $2.4 \times 10^9$  BTU).

#### Sodium Sulfate

Sodium sulfate is a by-product of sodium dichromate and other manufacturing processes. As such, no water-borne wastes are attributed to its production. Therefore, it is considered to be a zero effluent-zero treatment and control chemical with no additional energy requirements.

#### Sodium Metal

Sodium metal and chlorine are produced as coproducts in the Downs Cell process. Since the chlorine produced is handled similarly and has the same wastes as the mercury and diaphragm cell processes, only wastes specific to the Downs Cell and sodium production are included here. Table 62 gives the estimated cost effectiveness values for a 58 kkg/day (65 ton/day) fourteen year old plant (096).

TABLE 61 .

Water Effluent Treatment Costs

Inorganic Chemicals

Chemical: Sodium Dichromate (149 kkg/day (164 tons/day) Capacity)

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A B C D			
	A	B	C	D
Investment	100,000	1,000,000	1,800,000	1,800,000
Annual Costs:				
Interest + Taxes and Insurance	5,000	5,000	90,000	90,000
Depreciation	10,000	100,000	180,000	180,000
Operating and Maintenance Costs (excluding energy and power costs)	~0	560,000	610,000	610,000
Energy and Power Costs	~0	4,000	64,000	64,000
Total Annual Cost	15,000	669,000	944,000	944,000

#### Effluent Quality:

Effluent Constituents Parameters (Units) kg/kkg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels			
Total Suspended Solids	900(1800)	0.125(0.25)	0.125(0.25)	~0	~0
Total Dissolved Solids	88.5(177)	88.5(177)	88.5(177)	~0	~0
Chromium 6	-	-	0.0001(0.0002)	~0	~0

Level A -- Settling pond.

Level B -- Segregation and chemical treatment for chromium-6. Pond settling and discharge of clear effluent to surface water.

Level C -- Level B + evaporation to recover dissolved sodium chloride. Recovered sodium chloride costed as zero value. Closed loop operation.

TABLE 62.

Water Effluent Treatment Costs

Inorganic Chemicals

Chemical: Sodium Metal (58 kkg/day (65 tons/day) Capacity)

Treatment of Control Technologies Identified under Item III of the Scope of Work:

	A	B	C	D
Investment	0	400,000	700,000	0
Annual Costs:				
Interest + Taxes and Insurance	0	20,000	35,000	35,000
Depreciation	0	40,000	70,000	70,000
Operating and Maintenance Costs (excluding energy and power costs)	4,000	4,000	10,000	10,000
Energy and Power Costs	~0	~0	~0	~0
Total Annual Cost	4,000	64,000	115,000	115,000

Effluent Quality:

Effluent Constituents Parameters (Units)	Raw Waste Load	Resulting Effluent Levels			
kg/kkg (Pounds/Ton)					
Sodium Chloride	57.5(115)	57.5(115)	57.5(115)	~0	~0
Misc. Alkaline Salts	30(60)	30(60)	30(60)	~0	~0
Bricks, Anodes, Other Solids	~2.5(5)	0	0	0	~0

Level A -- Disposal of salts plus solids.

Level B -- Facilities for separating salts from solids.

Level C -- Containment, isolation and return of salts to brine system.

Costs for plant 096 to attain a zero water-borne waste effluent are \$2.47/kkg (\$2.25/ton) of sodium above initial expenditures of \$3.30 to \$4.40/kkg (\$3 to \$4/ton) of sodium, which is currently selling for \$412/kkg (\$375/ton).

Additional energy costs should be negligible.

## Sodium Silicate

The wastes from the sodium silicate manufacturing process are relatively small and closed loop operation has been achieved in plant 072.

For the purpose of developing cost effectiveness data plant 134 has been selected for Table 63 calculations. This plant is a ten year old, 72 kkg/day (80 ton/day) facility. Control and treatment costs are approximately \$1.00/kkg (\$0.90/ton) of product.

Additional energy costs using this approach are  $3.5 \times 10^9$  kg cal ( $14 \times 10^{10}$  BTU). For the total industry, additional energy requirements are  $8.4 \times 10^{10}$  kg cal ( $3.32 \times 10^{11}$  BTU).

A second approach using only Level A treatment and closing the loop bypasses both the energy requirements and most of the cost. This approach is used in plant 072. Treatment costs for this approach would be approximately \$0.22/kkg (\$0.20/ton) of product.

Costs for both approaches are reasonable. In view of the energy advantage for plant 072's approach, this recycle method should be favored.

## Sodium Sulfite

The wastes from the sodium sulfite processes are essentially sodium sulfite. Table 64 gives the cost effectiveness values for plant 168, a fifteen year old installation.

Costs for reducing the waste water discharge from plant 168 to zero are approximately \$2.75/kkg (\$2.50/ton) of product. If recovery of sodium sulfite is directed at the same stream which is now treated and directly discharged, there is a potential for \$25,000/yr profit. Plants not now treating or recovering sodium sulfite should explore this approach.

Additional energy required is approximately  $1.62 \times 10^9$  kg cal/yr ( $6.4 \times 10^9$  BTU/yr) or 24,200 l (6400 gal) of fuel oil /yr. For the entire industry this would be  $2.92 \times 10^{10}$  kg cal ( $1.16 \times 10^{11}$  BTU).

TABLE 63.  
Water Effluent Treatment Costs  
Inorganic Chemicals  
Chemical: Sodium Silicate (72 kkg/day (80 tons/day) Capacity)

Treatment of Control Technologies Identified under Item III of the Scope of Work:					
	A	B*	C*	D	
Investment	26,000	42,000	62,000	62,000	
Annual Costs:					
Interest + Taxes and Insurance	1,300	2,106	3,100	3,100	
Depreciation	2,600	4,200	6,200	6,200	
Operating and Maintenance Costs (excluding energy and power costs)	1,000	9,000	10,000	10,000	
Energy and Power Costs	~0	—	10,000	10,000	
Total Annual Cost	4,900	15,300	29,300	29,300	
Effluent Quality:					
Effluent Constituents Parameters (Units) kg/kkg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels			
Sodium Silicate	2(4)	2(4)	2(4)	0	0
Sodium Sulfate	2.5(5)	2.5(5)	2.5(5)	0	0
Filter Aids	2(4)	0	0	0	0
Sand	0.5(1)	0	0	0	0
Sodium Hydroxide	0.5(1)	0.5(1)	0	0	0
Level A -- Settling pond only.					
Level B -- Settling pond plus neutralization (existing good plant).					
Level C -- Evaporation to remove and recover dissolved solids + Levels A and B treatment. Sodium silicate recovered (exemplary plant).					

\*Note Level C is exemplary plant level in this table.

TABLE 64.  
Water Effluent Treatment Costs  
Inorganic Chemicals  
Chemical: Sodium Sulfite (45 kkg/day (50 ton/day) Capacity)

Treatment of Control Technologies Identified under Item III of the Scope of Work:				
	A	B	C	D
Investment	0	250,000	275,000	150,000
Annual Costs:				
Interest + Taxes and Insurance	0	12,500	13,750	7,500
Depreciation	0	25,000	27,500	15,000
Operating and Maintenance Costs (excluding energy and power costs)	0	10,000	12,000	5,000
Energy and Power Costs	0	2,000	7,000	6,000
Total Annual Cost	0	49,500	47,750	(25,000) Profit
Effluent Quality:				
Effluent Constituents Parameters (Units) kg/kkg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels		
Sodium Sulfate	—	—	29(58)	0
Sodium Sulfite	30.5(61)	30.5(61)	1.5(3)	0
Level A -- No treatment -- typical for industry.				
Level B -- Full treatment system, but dissolved solids still discharged.				
Level C -- Level B + evaporation recovery and sales of recovered product. Product value \$12,500.				
Level D -- Isolation and containment parts of complete system of Level B + evaporation to recover sodium sulfite. Product value is \$58,500.				



## Sulfuric Acid

The sulfuric acid (sulfur-burning) manufacturing process has no process wastes. The only water-borne wastes result from leaks, spills, air pollution control equipment, and ancillary operations such as cooling tower blowdowns and ion-exchange regenerants. Since cooling tower blowdowns and ion-exchange regenerants are not considered to be process waste water, they are not included here. Air pollution control equipment costs are presented for informational purposes.

Regen plants for making sulfuric acid from waste or spent acid are not covered in this study but are included in cost effectiveness development for informational purposes.

Exemplary sulfur-burning plant 141, a three year old, 360 kkg/day (400 ton/day) plant, was used as the model in Table 65.

Costs are less than \$0.10/kkg (\$0.10/ton) of product. Additional energy is negligible.

### Titanium Dioxide

#### a) Chloride process

Most chloride processes for titanium dioxide production use either rutile or "synthetic rutile" ore. One plant uses lower-grade ores but for the purposes of this cost effectiveness discussion, this process is considered to be on-site beneficiation plus a "synthetic rutile" process.

Currently, chloride process wastes are treated or disposed of by complete neutralization, deep-welling and ocean barging. For companies already ocean barging, cost run \$5.50 - \$11 kkg (\$5 to \$10 per ton) of titanium dioxide product. For those starting barging a location further from the ocean, or requiring extensive shore facilities, the costs may range from \$11 to \$22/kkg (\$10 to \$20/ton).

Deep-welling costs run from \$2.20 to \$5.50/kkg (\$2 to \$5/ton) of titanium dioxide product. Complete neutralization, on the other hand, is much more expensive. Table 66 shows the cost effectiveness development for this approach using ten year old 67 kkg/day (74 ton/day) exemplary plant 009 as the model.

Complete neutralization which is now done by plant 009 costs \$40/kkg (\$36/ton) differential over base treatment Level A.

Reduction to virtually zero discharge of wastes costs \$71/ kkg (\$64/ton) of product. Titanium dioxide sells for \$605 to \$627/kkg (\$550 to \$570/ton).

Additional energy costs are roughly estimated to be  $1.3 \times 10^{10}$  x  $10^{10}$  kg cal ( $5.0 \times 10^{10}$  BTU) for plant 009 and  $1.7 \times 10^{10}$  kg cal

TABLE 65.

Water Effluent Treatment Costs

Inorganic Chemicals

Chemical: Sulfuric Acid (Sulfur Burning)(360 kkg/day (400 tons/day) Capacity)

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B	C	D
Investment	50,000	100,000	160,000	160,000
Annual Costs:				
Interest + Taxes and Insurance	2,500	5,000	8,000	8,000
Depreciation	5,000	10,000	16,000	16,000
Operating and Maintenance Costs (excluding energy and power costs)	~0	~0	~0	~0
Energy and Power Costs	~0	~0	~0	~0
	7,500	15,000	24,000	24,000

#### Total Annual Cost

#### Effluent Quality:

Effluent Constituents Parameters (Units)	Raw Waste Load	Resulting Effluent Levels			
kg/kkg(Pounds/Ton)					
Spills, Leaks	1(2)	0.5(1)	0	0	0

#### Closed Cycle System

Level A -- Typical diking and containment.

Level B -- Good isolation and containment + Level A.

Level C -- Lined containment emergency pond -- 0.4 hectare (1 acre) + Level A and B.

TABLE 66.

## Water Effluent Treatment Costs

## Inorganic Chemicals

Chemical: Titanium Dioxide (Chloride Process), 67 kkg (74 ton) per day basis

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B	C	D
Investment	300,000	4,000,000	5,300,000	5,300,000
Annual Costs:				
Interest + Taxes and Insurance	15,000	200,000	265,000	265,000
Depreciation	30,000	400,000	530,000	530,000
Operating and Maintenance Costs (excluding energy and power costs)	10,000	390,000	890,000	890,000
Energy and Power Costs	~0	10,000	45,000	45,000
Total Annual Cost	55,000	1,000,000	1,730,000	1,730,000

## Effluent Quality:

Effluent Constituents Parameters (Units)	Raw Waste Load	Resulting Effluent Levels			
kg/kkg (Pounds/Ton)					
Iron Hydroxides	65(130)	65(130)	~0	~0	~0
Other metal oxides	65(130)	65(130)	~0	~0	~0
Ore	138(276)	~0	~0	~0	~0
Titanium hydroxides	25(50)	29(58)	~0	~0	~0
Hydrochloric Acid	227(454)	227(454)	~0	~0	~0
Titanium Dioxide	40.5(81)	~0	~0	~0	~0
Coke	23(46)	~0	~0	~0	~0
Soluble Chlorides and sulfates	-	-	315(630)	~0	~0

Level A -- Pond settling.

Level B -- Complete chemical treatment facility + land dumping of solid waste.

Level C -- Level B + specialty unit demineralization + evaporation of regenerant solution.

Level D -- Same as Level C.

( $6.75 \times 10^6$  BTU) for the entire industry using the same treatment.

## b) Sulfate process

The sulfate process for producing titanium dioxide has the heaviest water-borne waste load per ton of product of all the processes of this study. Of the approximately three kkg waste/kkg of product, two kkg are sulfuric acid. The model plant used is plant 142, a twenty-seven year old 108 kkg/day (120 ton/day) facility. Cost effectiveness is developed in Table 67.

Additional costs in going from typical Level A to virtually complete elimination of water-borne wastes are \$106/kkg (\$96/ton) or 10.5¢/kg (4.8¢/lb) of titanium dioxide produced. Going to Level C costs \$90/kkg (\$82/ton) or 9.0¢/kg (4.1¢/lb).

This is compared to \$8.80 to \$11.0/kkg (\$8 to \$10/ton) for ocean barging of strong acid wastes. Adding Level B costs of approximately \$11/kkg (\$10/ton) to this gives about \$22/kkg (\$20/ton) for removal of acidity and the largest portion of the wastes. Ocean barging, as mentioned for the chloride process, can range for new plants (or old plants not now using this disposal means) up to \$33/kkg (\$40/ton) or \$44/kkg (\$40/ton) overall waste costs. Thus, ocean barging costs about one-fourth to one-half that of complete neutralization.

Acid recovery is another attractive approach. Using a current EPA-support pilot plant as model for acid recovery, cost effectiveness is developed in Table 68. Additional costs for this approach are \$53/kkg (\$48/ton) of titanium dioxide produced for practically zero water-borne waste eliminating Level D. Without demineralization, additional costs above Level A are \$37.50/kkg (\$34/ton) or about one-half that for complete neutralization.

Required additional energy for complete neutralization plus demineralization and evaporation of regenerant is  $4.15 \times 10^{10}$  kg cal/yr ( $4.0 \times 10^9$  BTU/yr) for plant 142 and  $1.35 \times 10^{10}$  kg cal/yr ( $5.35 \times 10^9$  BTU/yr) for the industry (sulfate process).

Similar values for acid recovery are  $1.6 \times 10^{10}$  kg cal ( $6.3 \times 10^9$  BTU) for plant 142 and  $1.32 \times 10^{10}$  kg cal ( $5.2 \times 10^9$  BTU) for the industry.

TABLE 67.

Water Effluent Treatment Costs

Inorganic Chemicals

Chemical: Titanium Dioxide (Sulfate Process), 108 kkg (120 ton) per day basis

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B	C	D
Investment	100,000	150,000	11,200,000	11,500,000
Annual Costs:				
Interest + Taxes and Insurance	5,000	7,500	560,000	575,000
Depreciation	10,000	15,000	1,120,000	1,150,000
Operating and Maintenance Costs (excluding energy and power costs)	65,000	400,000	2,220,000	2,350,000
Energy and Power Costs	~0	~0	11,000	45,000
Total Annual Cost	80,000	422,500	4,011,000	4,120,000

## Effluent Quality:

Effluent Constituents Parameters (Units) kg/kg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels			
Sulfuric Acid	2025(4050)	2025(4050)	1745(3490)	~0	~0
Iron Sulfate	387(774)	387(774)	370(740)	~0	~0
Aluminum Sulfate	270(540)	270(540)	260(520)	~0	~0
Magnesium Sulfate	220(440)	220(440)	210(420)	~0	~0
Other metal sulfates	35(70)	35(70)	35(70)	~0	~0
Solid Wastes	210(420)	20(40)	20(40)	~0	~0
Soluble Calcium Sulfate	-	-	-	265(530)	~0

Level A -- Settling Pond

Level B -- Level A + neutralization of weak acid stream.

Level C -- Full neutralization.

Level D -- Level C + specialty system demineralization + evaporation of regenerant solution.

TABLE 68.

Water Effluent Treatment Costs (Acid Recovery Option)

Inorganic Chemicals

Chemical: Titanium Dioxide (Sulfate Process), 108kkg (120/ton) per day basis

Treatment of Control Technologies Identified under Item III of the Scope of Work:	A	B	C	D
Investment	100,000	150,000	4,000,000	5,500,000
Annual Costs:				
Interest + Taxes and Insurance	5,000	7,500	200,000	275,000
Depreciation	1,000	15,000	400,000	550,000
Operating and Maintenance Costs (excluding energy and power costs)	65,000	400,000	500,000	850,000
Energy and Power Costs	~0	~0	400,000	445,000
Total Annual Cost	71,000	422,500	1,500,000	2,120,000

## Effluent Quality:

Effluent Constituents Parameters (Units) kg/kg (Pounds/Ton)	Raw Waste Load	Resulting Effluent Levels			
Sulfuric Acid	2025(4050)	2025(4050)	1745(3490)	~0	
Iron Sulfate	387(774)	387(774)	370(740)	~0	~0
Aluminum Sulfate	270(540)	270(540)	260(520)	~0	~0
Magnesium Sulfate	220(440)	220(440)	210(420)	~0	~0
Titanium Sulfate	180(360)	180(360)	130(260)	~0	~0
Other metal sulfates	35(70)	35(70)	35(70)	~0	~0
Solid Wastes	210(420)	20(40)	20(40)	~0	~0
Soluble Calcium Sulfate	-	-	-	~200(~400)	~0

Level A -- Settling Ponds

Level B -- Level A + weak acid stream neutralization.

Level C -- Level B + acid recovery facilities.

Level D -- Level C + specialty system demineralization + evaporation of regenerant solution.



Summarizing the costs for rough comparison purposes gives:

Method	Cost/kgg (Cost/ton) Titanium Dioxide
Ocean barging and weak acid neutralization	\$22 (\$20)
Acid recovery	\$44 (\$40)
Total neutralization	\$88 (\$80)

Overlaps in costs can occur depending on specific circumstances. Since most of the neutralization products are insoluble calcium sulfate and metallic oxides and hydroxides, the complete neutralization of sulfate process wastes is a relatively "clean" process. Also, its simple tested technology reliability is attractive. Acid recovery is still in the development stage for the process described. Corrosion problems are the biggest current uncertainty. The cost of this approach is one-half that of complete neutralization, however, and there is no reason why technology know-how can not be brought to bear on this process.

#### GENERAL INFORMATION ON COST OF CONTROL AND TREATMENT SYSTEMS

Segregation of contaminated water streams from non-contaminated streams is the first step in water-borne waste abatement. Since the treatment costs normally depend on the volume of water to be treated more than the amount of waste, keeping the waste water volume small reduces costs and energy requirements. Spills, leaks and washdowns are small, but need to be contained and isolated.

Cost for segregation and containment vary depending on the size and complexity of the plant, volume and nature of the wastes, and the equipment employed.

Estimates of these costs based on information obtained from plant visits are given below. In general, small chemical plants produce 50 tons/day or less of product. However, this may vary significantly with the particular chemical.

Isolation of wastes containing mercury and chromium costs approximately \$200,000 to \$300,000. Large salt, acid and chlor-alkali plants also fall in a similar price range for isolation and containment costs. Older plants may be more difficult and expensive to modify than new facilities.

#### Isolation and Containment Costs

Purpose	Installations	Small Plants	Large Plants
Isolation	Trenches and sewers pipelines, sumps, catch basins, tanks and pumps	\$ 10,000- 100,000	\$100,000- 300,000
Containment	Dikes and curbing	\$ 5,000- 50,000	\$ 50,000- 200,000
Isolation	Non-contact heat-exchangers	\$ 50,000	\$100,000- 500,000

Barometric condensers are the most common source of cooling water contamination. Barometric condensers are now being replaced by non-contact heat exchangers in various inorganic chemical plants.

#### Chemical Treatment Systems

##### Equipment Costs

These systems, consisting of chemical reactors, clarifiers, thickeners, and filters or centrifuges, are designed as integral units for complete waste treatment. Installed equipment costs for chemical treatment systems as a function of capacity are summarized below:

Capacity cu m/day (gal/day)	Reaction Tanks, \$	Clarifiers and Thick- eners, \$	Filters or Centrifuges, \$	Total* Costs \$
38 (10,000)	15,000	15,000	25,000	60,000
379 (100,000)	25,000	40,000	25,000	150,000
3785 (1,000,000)	37,500	75,000	200,000	500,000
37850 (10,000,000)	50,000	200,000	750,000	2,000,000

\*Includes engineering, land preparation, and installation. Does not include land cost, storage tanks and disposal facilities, or other auxiliary equipment.

These costs are for light slurry loads. For heavy slurry loads, such as for titanium dioxide wastes, overall costs are several times greater.

#### Chemical Costs

The costs for chemical treatments cannot be generalized. Most of the chemicals used, however, are for neutralizations. Chemical treatments costs depend on the chemical used and the amount

required, which varies with the particular situation. The unit cost of the chemical is usually known. Whenever feasible, neutralization of alkaline wastes is done with sulfuric acid. As shown in Table 69, sulfuric acid costs only 30 to 40 percent as much as hydrochloric and nitric acid. In other words, a dollars worth of sulfuric acid will neutralize 2.5 to 3.5 times as much alkalinity as a dollars worth of the other two acids. Cost for sulfuric acid is approximately \$33/kg (\$30/ton).

Limestone and lime are commonly used to neutralize acidic waste streams. Limestone is the lower cost material at \$7-11/kg (\$6-10/ton); but suffers the disadvantage of slower reaction, high impurities, and lower obtainable pH. Lime costs are approximately \$22/kg. Ammonia and sodium hydroxide are far more expensive than lime or limestone, with 50 percent sodium hydroxide at \$121/kg (\$110/ton) (100 percent basis), it can be seen why lime is preferable in most cases.

For small usage or where solubility or character of precipitate is important, caustic soda or ammonia may still be employed.

Neutralizations with waste acids or bases can change the whole cost structure. Waste sulfuric acid is often available at either no cost or the cost of freight. Waste lime, caustic soda or ammonia can sometimes be obtained at similar low costs.

Costs for neutralizations and other chemical reactions are simply determined for special applications by multiplying the cost/weight of the neutralizing or reacting chemical by the weight stoichiometrically required. Where specific experience is available, it may have been found that 10 to 20 percent excess over stoichiometric quantities are needed. In rare cases, several-fold excesses may be used to ensure complete reaction.

#### Settling Ponds and Vessels

Ponds for storage, emergency discharge and containment, settling of suspended solids, or solar evaporation, are the most commonly employed treatment and control facility in the inorganic chemical industry. Two categories, unlined ponds and lined ponds, are summarized in the tables and figures of this section.

A third category, tanks and vessels such as thickeners and clarifiers, are not widely used at present in the inorganic chemical industry as contrasted to other chemical industries and sanitary treatment facilities. As land becomes more costly and unavailable and treatment and control requirements change, open tanks and vessels may see increased use. Cost information on equipment of this type has already been given in the chemical treatment section.

TABLE 69. Comparison of Chemicals for Waste Neutralization

Alkaline Wastes		Relative Chemical Cost*, \$	kg*** Req'd/kg Alkali**		
Neutralizing Material			CaCO <sub>3</sub>	Ca(OH) <sub>2</sub>	NaOH
Sulfuric Acid	(50° Be)	1.00	1260	1700	1580
Hydrochloric Acid	(20° Be)	2.57	2320	3140	2500
Nitric Acid	(39.5° Be)	3.51	2100	2840	2630

Acid Wastes		Cost*, \$	kg*** Req'd/kg Acid**		
Neutralizing Material			H <sub>2</sub> SO <sub>4</sub>	HCl	HNO <sub>3</sub>
Lump limestone, high Ca		1.16	1100	1480	860
Lump limestone, dolomitic		1.00	940	1270	730
Pulv. limestone, high Ca		1.59	1100	1480	860
Pulv. limestone, dolomitic		1.37	940	1270	730
Hydrated lime, high Ca		3.06	790	1070	620
Hydrated lime, dolomitic		2.50	650	870	510
Pebble lime, high Ca		2.07	600	800	460
Pebble lime, dolomitic		1.87	540	730	420
Pulv. quicklime, high Ca		2.18	600	800	460
Pulv. quicklime, dolomitic		1.97	540	730	420
Sodium bicarbonate		20.65	1730	2330	1350
Soda ash		13.08	1190	1600	930
Caustic soda (50%)		9.96	1640	2200	1270
Ammonia (anhyd.)		5.90	350	470	270
Magnesium oxide		3.90	420	560	330

\*Delivered cost including freight.

\*\*Commodity weight.

\*\*\*To convert numbers to lbs. req'd/100 lbs alkali or acid, multiply x 0.1.



## Unlined Ponds

The costs of constructing unlined ponds differ widely depending on the circumstances. Since they cover large areas, the cost of the land itself is a factor. Building a 200 hectare (500 ac) pond on prime industrial land may cost \$1 to 5 million just for the land itself. No provision is made in this analysis, however, for such costs. It is assumed that the land value is not a large portion of the cost. For small ponds of less than 4 to 20 ha (10 to 50 ac) and land values of \$250 to \$625/ha (\$100 to \$250/ac), this assumption is good, as will be seen from the magnitude of the other costs.

Construction costs vary widely depending on the circumstances. Use is often made of natural pits, valleys, ponds, lakes, etc., for minor alterations, such as damming, dike building and leveling. Excavation is easier in some localities than others.

Pond size is also a major cost factor. Small ponds may be dug and the excavated dirt used for dikes. Large ponds are usually diked or dammed.

Assuming equal depths of two ponds, one large and one small, the volume increases as the square while the dike length (and earth moving) is increasing only linearly. Therefore, costs will be developed for small ponds and then for large ones.

Small pond capital costs are given in Figure 64.

Large pond costs developed from reference (27) are shown in Figure 65. Undoubtedly, many of these installations made use of natural topography (lakes, basins, etc.) to avoid as much excavation as possible. Nevertheless, the general cost levels and trends may be seen. As would be expected from the diking costs varying by the square root of the area, the pond costs per hectare above 200 ha (500 ac) change very slowly.

## Lined Ponds

To avoid excessive liquid seepage, ponds are often lined with clay, concrete or other substances. Recently, however, new lining materials have come into use -- rubber and plastic sheeting.

Essentially, costs for pond construction are the same as for unlined ponds except for the sheeting material and installation. Therefore, the costs may be estimated by adding the installed liner costs to the previously determined costs for unlined ponds. The material costs for the lining range from \$1.00 to \$6.00/sq m (10¢ to 60¢/sq ft), depending on the material selected and the thickness of the sheet. (30) Although thicknesses as low as 250 microns (10 mils) have been discussed, (31) the most used thickness appears to be 750 micron (30 mils). For 750 micron (30 mils) PVC liners, the installed cost is approximately \$2.00/sq m.

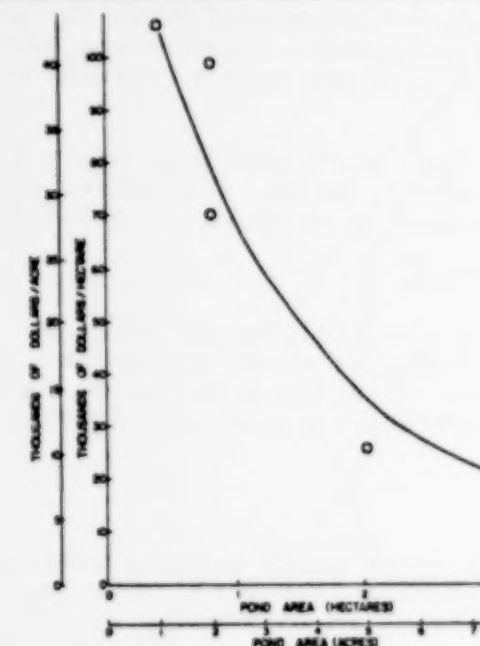


FIGURE 64  
CAPITAL COSTS FOR SMALL UNLINED PONDS  
(REFERENCE (28), (29), AND (30))

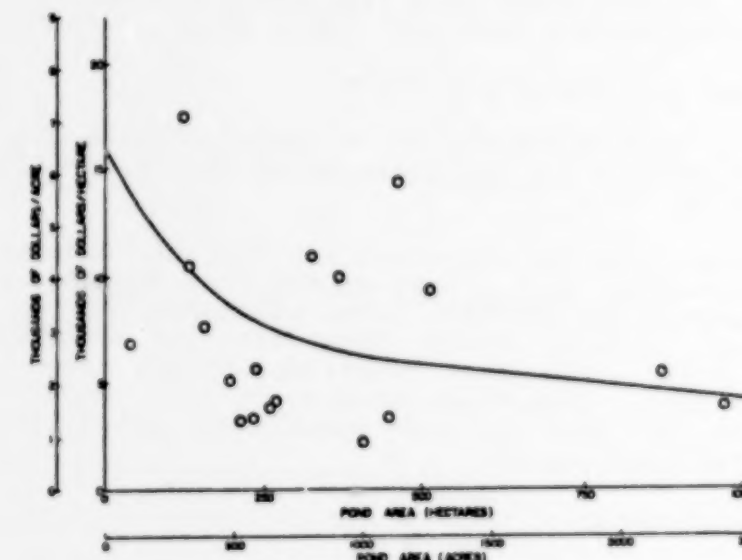


FIGURE 65  
CAPITAL COSTS FOR LARGE UNLINED PONDS  
(REFERENCE (27))



The construction costs for small lined ponds are given in Figure 66. These values may be conservative as far as film costs are concerned. For large ponds, lined costs have been estimated by adding \$2.00/sq m (20¢/sq ft) to the unlined costs. The results are shown in Figure 67.

Since a 200 ha (500 ac) lined pond costs \$4 to 6 million this approach for large scale waste treatment and/or storage will require careful investigation before proceeding.

#### Solar Evaporation Ponds

Table 70 gives the costs for solar ponds as a function of evaporative capacity. Table 71 gives costs per 3785 liters (1000 gallons) calculated from Table 70 for comparison with treatment costs for other processes. A pond and liner life of 20 years was assumed.

#### Carbon Adsorption

There are a few instances where organic materials are present in the inorganic chemicals industry water wastes. These organic materials may be handled in many cases by conventional biological digestion or they may be treated by methods such as carbon adsorption.

Installation costs range from 5¢ to 20¢/3785 l (1000 gal) treated. A cost of 15¢ was chosen as representative. This cost includes 5 percent loss of efficiency upon carbon regeneration.

Combining capital costs from Figures 68 and operating costs from above, yields overall treatment costs as shown in Figure 69.

#### Ion Exchange and Demineralization

Ion-exchange and demineralization water treatments are widely used, particularly for pretreatment of boiler, cooling tower, and process feeds.

Ion exchange, as its name implies, replaces undesired ions with less objectionable ones. Some of the ions removed in this way include magnesium, calcium, iron, manganese, carbonate, nitrate, and sulfate. Usually these ions are replaced by sodium or chloride ions. The total quantities of dissolved solids remain almost the same. Demineralizations, on the other hand, by a combination of ion exchange operations, actually remove almost all the dissolved solids.

#### Ion Exchange Costs

Ion exchange units are generally restricted to treating waste waters with low concentrations of dissolved solids. Two common

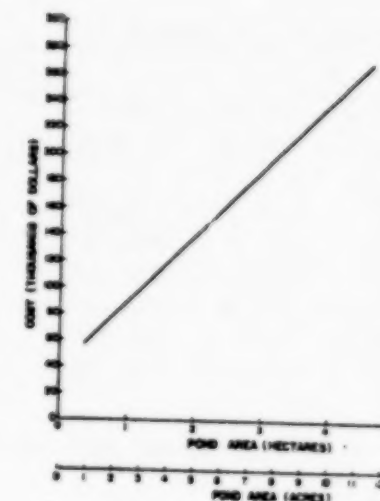


FIGURE 66  
CONSTRUCTION COST OF SMALL LINED PONDS  
(REFERENCE (30))

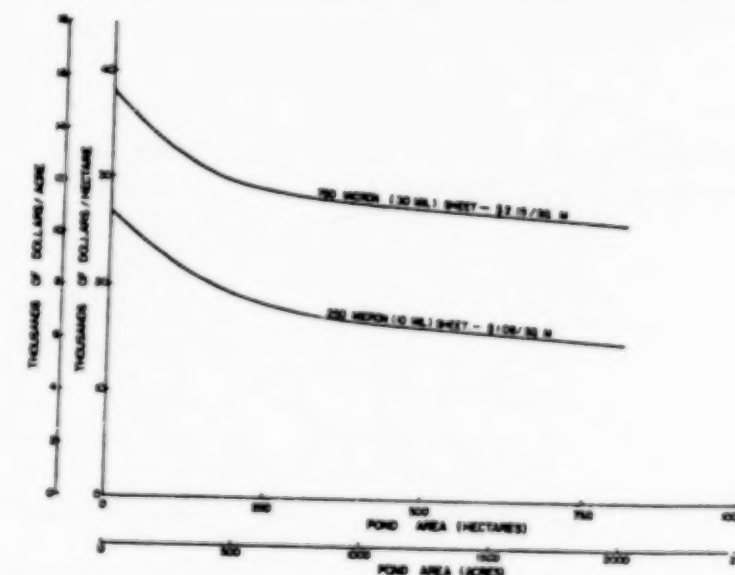


FIGURE 67  
CAPITAL COSTS FOR LARGE LINED PONDS

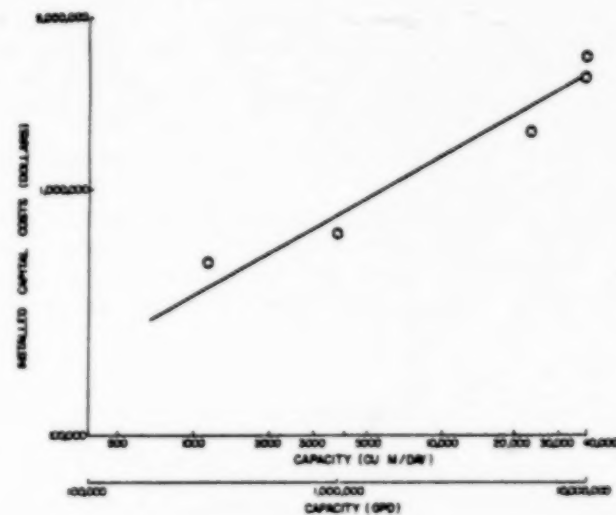


FIGURE 68  
INSTALLED CAPITAL COST FOR  
CARBON ADSORPTION EQUIPMENT

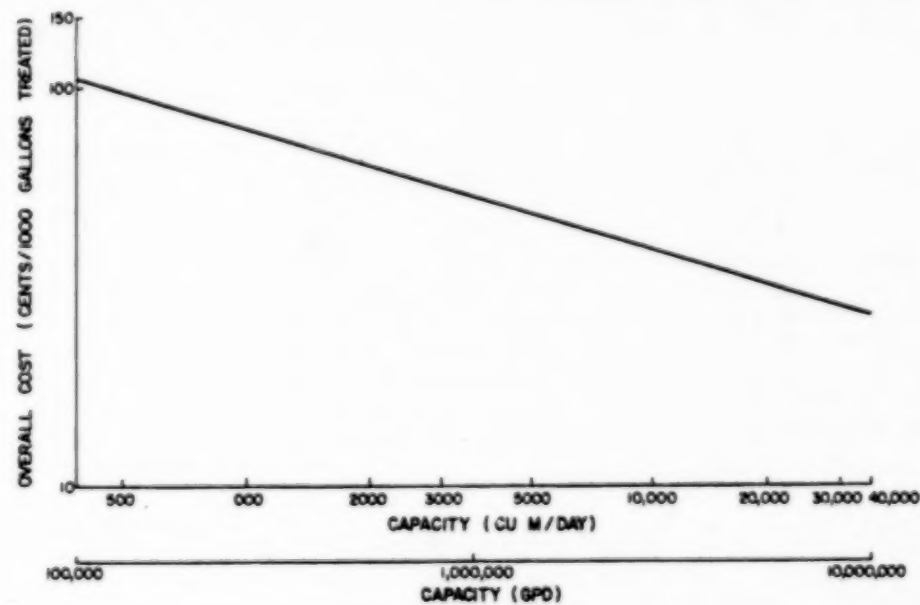


FIGURE 69  
OVERALL COSTS FOR CARBON ADSORPTION

TABLE 70. Capital Costs for Lined Solar Evaporation Ponds as a Function of Capacity\*

Capacity cu m/day (GPD)	Evaporation--Rainfall Differential					
	2 Ft.		4 Ft.		6 Ft.	
	Hectare (Acres)	Capital Costs	Hectare (Acres)	Capital Costs	Hectare (Acres)	Capital Costs
38 (10,000)	2.2 (5.6)	150,000	1.1 (2.8)	95,000	0.8 (1.9)	80,000
189 (50,000)	11.2 (28)	420,000	5.6 (14)	212,000*	3.7 (9.3)	220,000*
378 (100,000)	22 (56)	820,000	11.2 (28)	470,000	7.5 (18.7)	282,000
945 (250,000)	56 (140)	1,960,000	28 (70)	1,010,000	18.7 (46.7)	690,000
1890 (500,000)	112 (280)	3,700,000	56 (140)	1,960,000	37.3 (93.3)	1,350,000
3785 (1,000,000)	220 (560)	6,650,000	112 (280)	3,700,000	74.8 (187)	2,570,000

\*Ponds of 10 acres and under taken from Figure 74; those over 10 acres taken from Figure 75.

TABLE 71. Costs for Solar Evaporative Pond Disposal

Evaporative Capacity cu m/day (GPD)	20-Year Pond Life		
	Cost, ¢/3785 liters (¢/1,000 Gal.)		
	Evaporation-Rainfall Differential		
	2 ft/yr	4 ft/yr	6 ft/yr
38 (10,000)	214	136	114
379 (100,000)	117	67	40
3785 (1,000,000)	95	53	37

treatment methods are: (1) Sodium-hydrogen zeolite dealkalizers  
(2) Zeolite softeners

Estimated costs of ion-exchange operations as a function of dissolved solids concentration are shown below:

Total Dissolved Solids (mg/l)	Zeolite Softening, \$/3785 l (\$/1000 gal)	Sodium-Hydrogen Dealkalizer, \$/3785 l (\$/1000 gal)
200	5.7	6.4
500	10.8	9.5
750	15.0	12.2

While these values are only approximations, they do show that zeolite "softening" or ion exchange with sodium chloride or sodium chloride plus sulfuric acid is fairly low in cost even at the 750 mg/l total dissolved solids level. Ion exchange does not remove dissolved solids from waste water. Therefore, ion exchange units produce regenerant wastes which require disposal. With these considerations, ion exchange units are generally used only for certain specific harmful ion situations.

#### Demineralization Costs

The cost of demineralization equipment itself is fairly consistent for the low solids fixed bed units used for most applications. For the specialty systems described in Section VII, particularly at solids concentrations above 1000 mg/l, the costs are significantly higher for a given capacity. Both the special nature of these units and the influence of the higher resin volumes required to take the increased loading increase capital costs. Installed capital costs can also differ greatly depending on land availability, pretreatment facilities needed, buildings, storage tanks, and engineering and contractor costs. The installed capital costs developed in this section have been adjusted using 33 percent of equipment costs for installation and six percent increase per year in equipment costs. All values are in 1973 dollars. They do not include resin costs which are covered in operating costs. Values for capital costs were taken from literature references. Average values are plotted in Figure 70.

Generally, installed capital costs for conventional demineralization units are about one-half the cost for reverse osmosis installations with similar capacities.

The operating costs for demineralizations are made up of the costs of: (1) Resin; (2) Chemicals; (3) Labor and Maintenance.

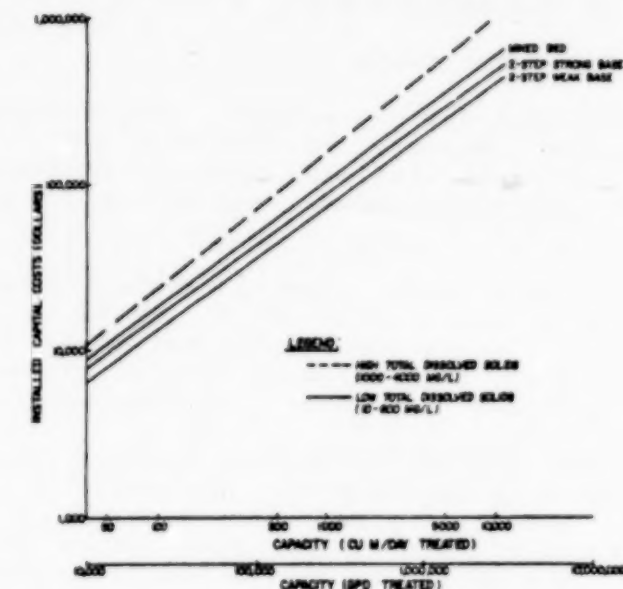


FIGURE 70  
INSTALLED CAPITAL COST vs. CAPACITY  
FOR DEMINERALIZATION

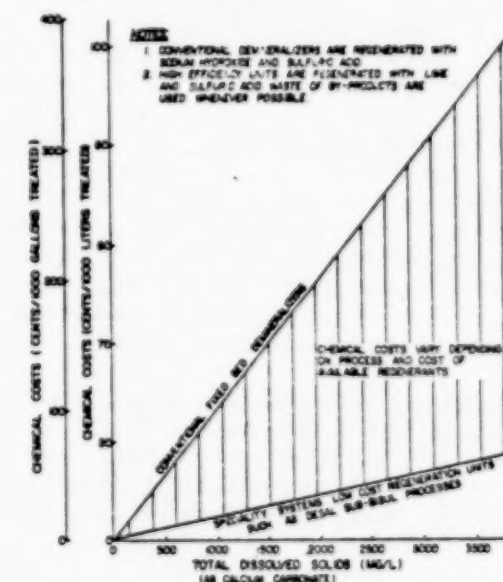


FIGURE 71  
CHEMICAL COSTS FOR DEMINERALIZATION



For the higher dissolved solids levels, chemical costs are the primary expense. These costs are shown in Figure 71. Overall costs are given in Tables 72 and 73.

#### Reverse Osmosis Treatment Costs

The costs involved with waste treatment using reverse osmosis are given comprehensive coverage in reference (49). The costs for reverse osmosis treatment include capital equipment, membrane replacement, pretreatment, power and labor plus maintenance materials.

The capital costs for reverse osmosis installations vary with plant size. Small units cost \$1.00 to \$1.50 per 3.78 l/day (gal/day) while large units lower this cost to \$0.50 or less per 3.78 l/day as shown in Figures 72 and 73. These costs do not include either extensive pretreatment or disposal facilities.

The selection of the membrane material, either sheet or hollow fiber, is governed by the nature of the waste to be treated and the product water quality desired. In general, tighter (small pore size) membranes have lower flux rates than more open structured ones. Therefore, to obtain low total dissolved solids product water, the area required for treatment will be significantly higher than for an allowable high total dissolved solids product water. In turn, the increased membrane surface area will increase the capital and membrane replacement costs. This correlation is shown in Figure 74.

Membrane life is one of the major factors of operating costs. Currently membrane life appears to be one to three years, with the average shifted toward the one to two year interval for replacement. This short and variable life has restricted use of reverse osmosis in many otherwise logical applications.

Since modules constitute one-third to one-half of the capital equipment costs, the life of the modules is critical. Unfortunately, module performance and life are difficult features to predict and control. For this reason, cost developments in this section are based on a two year life. As application experience increases, improved membrane life will significantly reduce operating costs. Table 74 summarizes membrane replacement costs for a membrane life of two to three years.

Various chemical pretreatments are required to prepare feedwater for passage through the membrane units. Included in these pretreatments are pH adjustment, such as acid addition to eliminate carbonate scaling, sulfate scaling control through addition of sodium hexametaphosphate, and chlorination for organics.

TABLE 72. Overall Costs for Demineralization

FIXED BED 2-STEP DEMINERALIZATION						
Capacity Treated cu m/day(GPD)	Installed Capital		Resin Costs ¢/1000 gallons or 3785 liters	Chemical Costs ¢/1000 gallons or 3785 liters	Labor and Maintenance Costs ¢/1000 gallons or 3785 liters	Overall Costs ¢/1000 gallons or 3785 liters
	Amortization ¢/1000 gallons or 3785 liters					
38(10,000) 378(100,000) 3785(1,000,000)	26.3	100 mg/liter, Total Dissolved Solids				
	16.3	3.2	10	1.8	41.3	
	8.2	3.2	10	1.1	30.6	
38(10,000) 378(100,000) 3785(1,000,000)	26.3	3.2	50	1.8	81.3	
	16.3	3.2	50	1.1	70.6	
	8.2	3.2	50	0.5	61.9	
38(10,000) 378(100,000) 3785(1,000,000)	26.3	1000 mg/liter, Total Dissolved Solids				
	16.3	3.2	100	1.8	131.3	
	8.2	3.2	100	1.1	120.6	
38(10,000) 378(100,000) 3785(1,000,000)	26.3	3.2	100	0.5	111.9	
	16.3	3.2	200	1.8	234.5	
	8.2	3.2	200	1.1	223.8	
38(10,000) 378(100,000) 3785(1,000,000)	26.3	6.4*	200	0.5	215.1	
	16.3	6.4*	200	1.8	234.5	
	8.2	6.4*	200	1.1	223.8	

\*Double resin cost assumed for increased loading.

TABLE 73. Overall Costs for Demineralization

SPECIALTY PROCESSES -- High Efficiency-Low Cost Regeneration Units

Capacity Treated cu m/day(GPD)	Capital	Resin	Chemical	Labor Maintenance Costs ¢/1000 gallons or 3785 liters	Overall Costs ¢/1000 gallons or 3785 liters
	Amortization ¢/1000 gallons or 3785 liters	Costs ¢/1000 gallons or 3785 liters	Costs ¢/1000 gallons or 3785 liters		
<u>1000 mg/l , Total Dissolved Solids</u>					
38( 10,000)	43	3.2	17	2.9	66.1
379(100,000)	21.4	3.2	17	1.4	43.0
3785(1,000,000)	12.5	3.2	17	0.8	33.5
<u>2000 mg/l , Total Dissolved Solids</u>					
38(10,000)	43	6.4*	33	2.9	85.3
379(100,000)	21.4	6.4*	33	1.4	62.2
3785(1,000,000)	12.5	6.4*	33	0.8	52.7
<u>3500 mg/l , Total Dissolved Solids</u>					
38(10,000)	43	12.8**	60	2.9	118.7
379(100,000)	21.4	12.8**	60	1.4	95.6
3785(1,000,000)	12.5	12.8**	60	0.8	86.1

\*Double resin cost assumed for increased loading.

\*\*Four times low solids resin costs assumed for this very heavy loading.

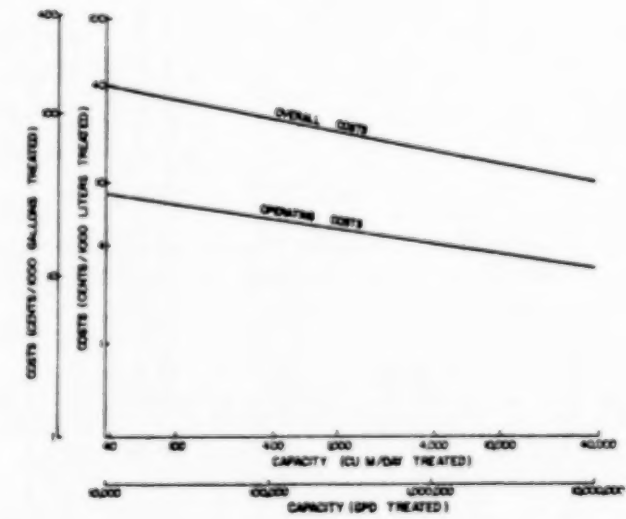


FIGURE 73  
COSTS FOR REVERSE OSMOSIS TREATMENT

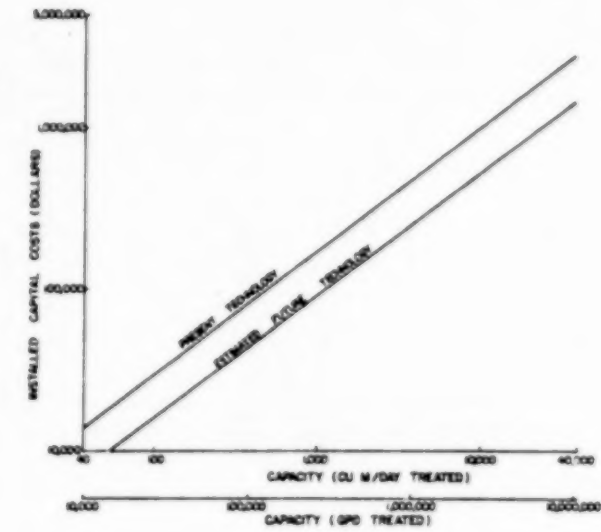


FIGURE 72  
INSTALLED CAPITAL COSTS FOR  
REVERSE OSMOSIS EQUIPMENT

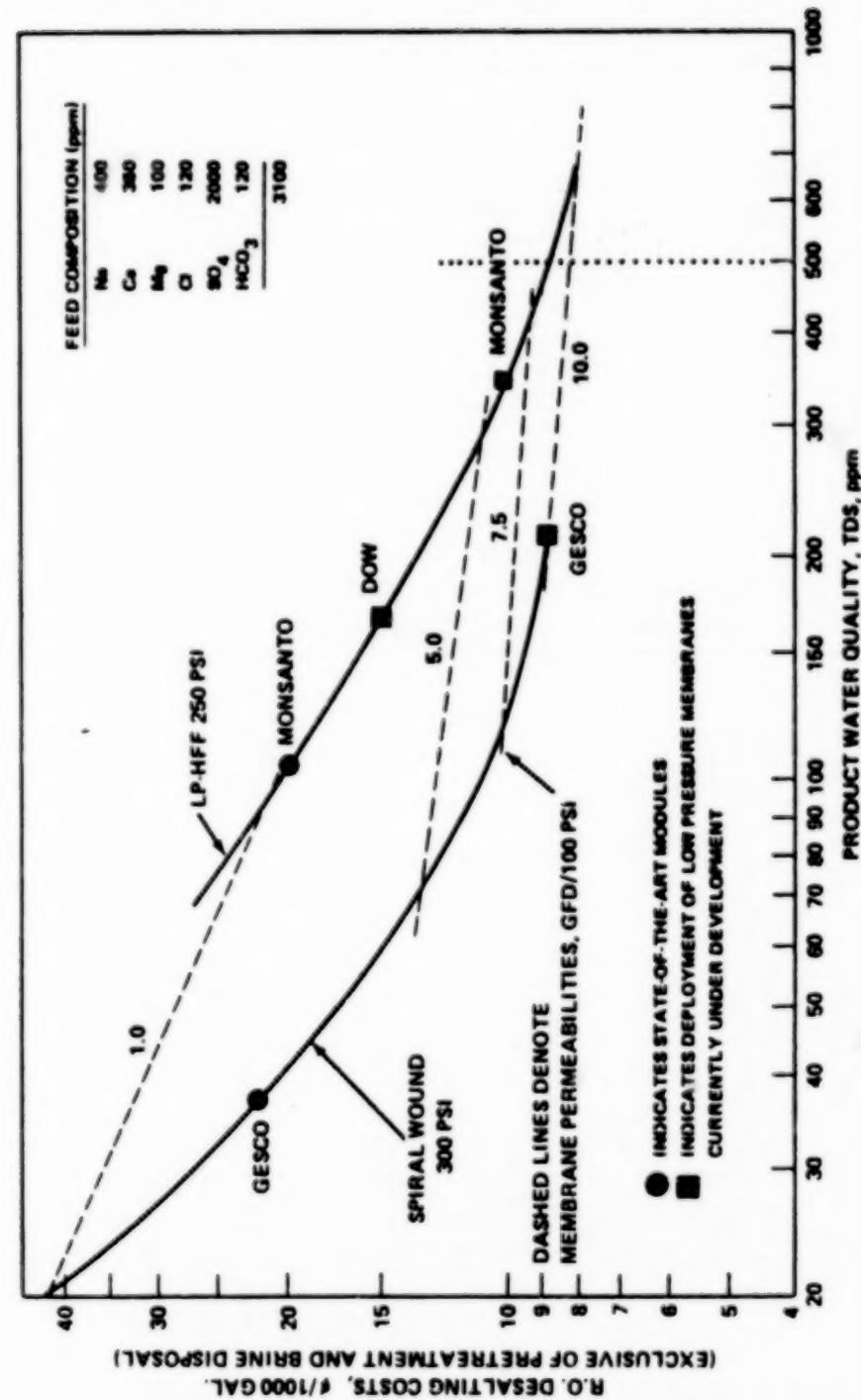


FIGURE 74. TRADE-OFF BETWEEN MEMBRANE PERMEABILITY (FLUX) AND SELECTIVITY (REJECTION AND PRODUCT WATER QUALITY) FOR CELLULOSE ACETATE BASE MEMBRANES (10 MGD PLANT @ 55% RECOVERY, 3100 ppm TDS FEED)

TABLE 74. Reverse Osmosis -- Membrane Replacement Costs

Volume Treated		\$/1000 gal. or 3785 l Treated			
		2 Yr. Life		3 Yr. Life	
cu m/day	GPD	Present	Future	Present	Future
38	10,000	45	22	30	15
95	25,000	45	22	30	15
189	50,000	45	22	30	15
379	100,000	38	20	25	13
945	250,000	38	20	25	13
1,890	500,000	30	15	20	10
3,785	1,000,000	30	15	20	10
18,900	5,000,000	22	12	15	8
37,850	10,000,000	15	8	10	5

Taken from Reference (49), p. 108. Converted to cu m/day and GPD treated basis plus two (2) year life adjustment.

TABLE 75. Reverse Osmosis -- Operating Costs

Volume Treated		\$/1000 gal. or 3785 l Treated			
		Power*	Chemicals**	Labor Plus Maintenance	Total
cu m/day	GPD			Materials	Cost
38	10,000	6	4	28	38
95	25,000	6	4	20	30
189	50,000	6	4	15	25
379	100,000	6	4	10	20
945	250,000	6	4	7	17
1,890	500,000	6	4	5	15
3,785	1,000,000	6	4	4	14
18,900	5,000,000	6	4	2	12
37,850	10,000,000	6	4	15	11.5

\*At 1¢ per kwhr.

\*\*Will vary depending on pretreatment required.

\*\*\*Additional breakdowns in reference cited above.



A low energy requirement is one of the major advantages of the reverse osmosis process. The primary energy requirement is for high pressure pumps.

The operating costs are summarized in Table 75. Figure 73 combines the information developed into overall reverse osmosis treatment costs. These values are based on conservative engineering and industrial calculations and assumptions, assuming straight line ten year depreciation, six percent money and membrane life of two years.

Evaporation Costs

Although there are many different designs and variations of evaporative equipment, four basic types, as described in Section VII, are commonly employed in the inorganic chemicals manufacturing industry. They are: (1) single-effect evaporators; (2) multi-effect evaporators; (3) high efficiency vertical tube and multi-effect flash evaporators; and (4) low energy specialty evaporators. Costs for these types of equipment and their operation are given in the following subsections.

Each type of evaporator has its individual operating specifications, as shown in Table 76. Figure 75 compares the energy requirements of each evaporator type with other treatment techniques as a function of dissolved solids concentration.

The selection of evaporative equipment depends on the job requirements. For high volume, low solids stream concentrations the VTE, or multi-flash type units should be used. Ninety percent or more of the water can be recovered as high purity product with relatively low energy requirements. The remaining five to ten percent can be more economically removed by recirculating evaporators or dryers. Although energy requirements are high per kg of water removed for single effect evaporators and dryers, the total energy requirement and capital costs for this step are relatively low. High volume, high solids content streams may be handled similarly except that conventional multi-effect evaporators should be used for the first concentration.

Low Energy Specialty Evaporator Costs

Capital costs for a low energy specialty unit, the flat plate vapor compression evaporator, are given below.

Capacity cu m/day (gal/day)	Installed Capital Costs, \$
379 (100,000)	635,000
850 (225,000)	1,350,000
1890 (500,000)	2,500,000

TABLE 76. Evaporator Characteristics

Character- istics	Re- circulative Evaporator	Multi- effect	High Efficiency Vertical Tube Evaporator	Low Energy Specialty Evaporator
Effects	1-3	2-6	10-20	15-30
Evaporative energy, kg cal/kg (Btu/lb)	222-555 (400-1000)	100-333 (180-600)	42-56 (75-100)	19-56 (35-100)
Optimum concentration range, % by weight of solids	20 to max.	10-50	1-10	1-10
Ability to handle heavy crystallizing or suspended solids load	Excellent	Good, can be easily equipped for re- circulation	Poor, not operable	Good, for calcium sulfate and other slurries
Optimum capacity range	Best for small capa- city below 5000 GPD	Good over wide capa- city range 10,000- 2,000,000 GPD	Mainly for high capa- city more than 1,000,000 GPD	Mainly for high capa- city more than 100,000 GPD
General costs	Relatively low	Inter- mediate	High	Highest

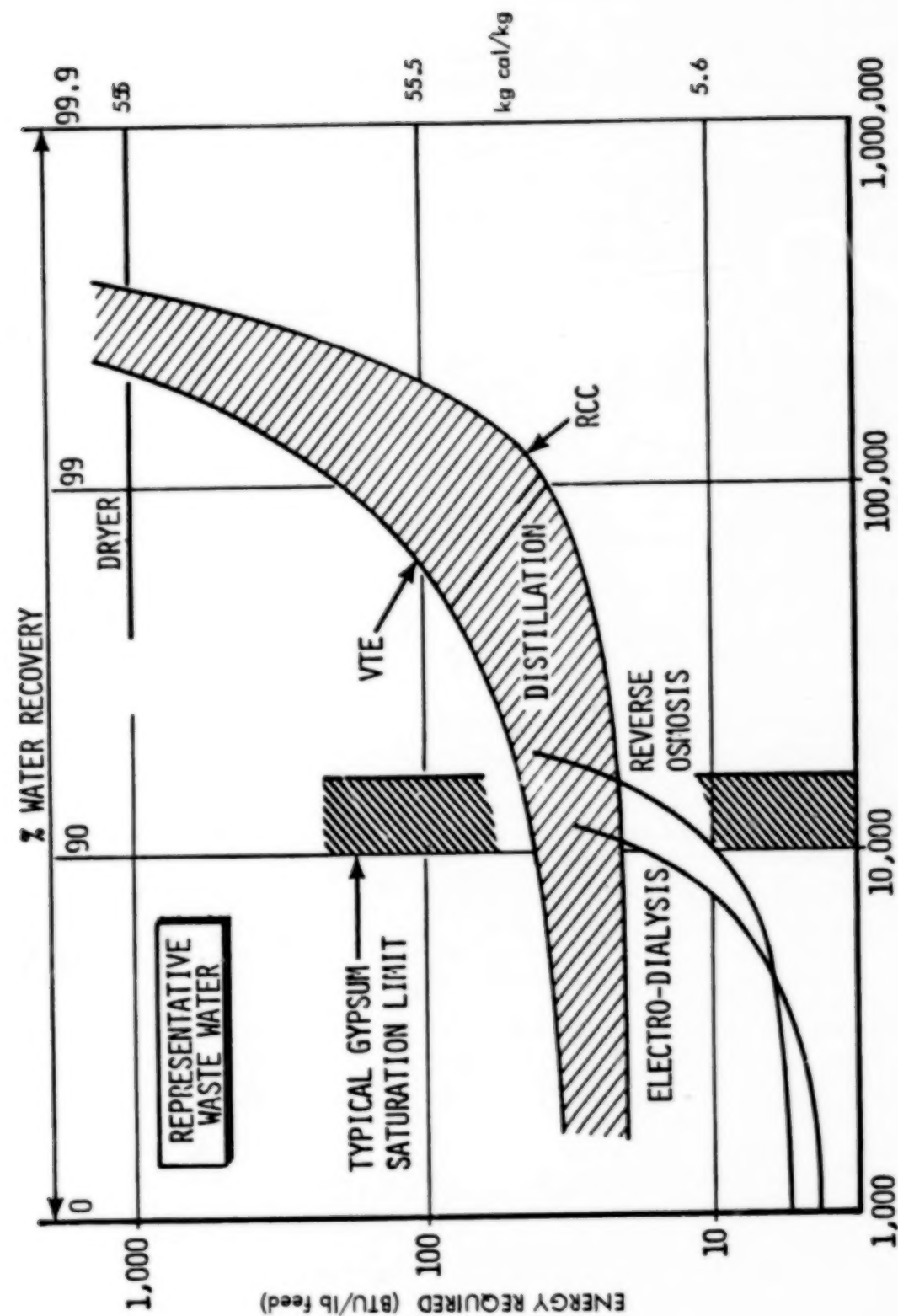


FIGURE 75: ENERGY COMPARISON FOR DISSOLVED SOLIDS REMOVAL

Larger capacities are made up of multiple small units. Operating expenses include costs for electric power, pretreatment chemicals, and labor.

Unlike most evaporators, this unit uses an electrically driven compressor instead of steam for its energy. Therefore, operating cost is directly influenced by the electrical power costs in the area. This cost may range from \$0.003/kwhr to over \$0.01/kwhr. For industrial applications, operating power costs are taken as \$0.01/kwhr. The amount of power required depends on the specific operating conditions. The following table gives estimated power as a function of the concentration of total dissolved solids in the concentrate.

Concentrate TDS* (mg/l)	kwhr/1,000 gal or 3785 l Treated
10,000	60
50,000	65
100,000	100
200,000	250

\*Total solids, including those suspended in the slurry, may be several times greater than the dissolved solids.

Operating and overall costs in \$/3785 liters (1000 gallons) for an 850 cu m/day (225,000 gpd) unit are given below:

Concentrate TDS*, mg/l	Power \$/3785 l (\$/1000 gal)	Chemicals \$/3785 l (\$/1000 gal)	Operation and Maintenance \$/3785 l (\$/1000 gal)	Total \$/3785 l (\$/1000 gal)
10,000	60	3	52	115
50,000	65	3	52	120
100,000	100	3	52	155
200,000	250	3	52	305

\*Since sparingly soluble water contaminants such as calcium sulfate and silica precipitate with concentration, total solids are usually much higher.

Concentrate TDS mg/l	Capital \$/1,000 gal or 3785 l	Operation \$/1,000 gal or 3785 l	Total \$/1,000 gal or 3785 l
10,000	257	115	327
50,000	257	120	377
100,000	257	155	412
200,000	257	305	562

These overall cost values are consistent with the basis used for other calculations of this report -- industrial 10 year depreciations and higher cost electric power than would be available to many current users. Low cost power and 35 year capital writeoffs would bring the overall costs down to approximately \$2.00/1,000 gallons or 3785 l treated.

It should also be emphasized that the power requirement correlation with total dissolved solids neglects the suspended solids portion of the recirculated slurry. Since many dissolved solids such as calcium sulfate are only sparingly soluble in water, concentration causes them to precipitate and form slurries. The unit is designed to handle such slurries up to total solids contents of 35 to 50 percent (at which point the total dissolved solids might be one percent or 10,000 mg/l). The critical difference here is that dissolved solids raise the boiling point of the solution, whereas suspended solids do not. The ability to handle slurries is one of the key technology advantages over multi-flash and vertical tube evaporators which are discussed next.

Vertical tube, multi-stage flash, and other high efficiency evaporators have been used in units to recover pure water from salt or brackish sources. Installed capital costs are shown in Figure 76 and operating and overall costs are given in Figure 77.

#### Conventional Multi-Effect Evaporators

For the heavy-duty, very high solids evaporations, industrial type multi-effect evaporators are commonly used. The inorganic salts in sea water and inorganic chemical industry are very corrosive. Even cupro-nickel and stainless steel alloys may not be sufficient for many of the solutions involved. Therefore, for this section, costs are given for solid nickel, titanium and tantalum materials, as well as stainless steel. Nickel construction raises the cost significantly, but will provide the reliable service required for industrial applications.

In selecting the optimum number of effects, a balance has to be made between equipment costs and operating costs. If the addition of an effect will not pay for itself in lower steam costs within approximately three years, the effect will probably not be added. It is rare that more than six or seven effects can be justified in this manner. (This is particularly true because of the high dissolved solid solutions or waste involved). Figures 78 and 79 show the interrelationships between number of effects and capital cost and steam usage, respectively.

Capital costs may be calculated rather quickly and directly from Figure 80:

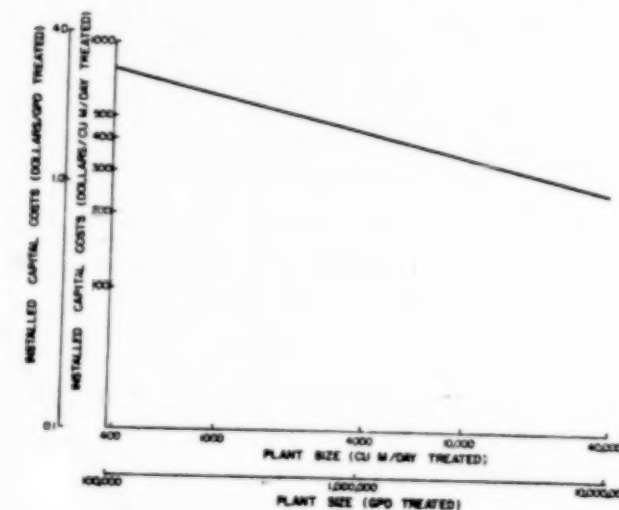


FIGURE 76  
INSTALLED CAPITAL COSTS vs. CAPACITY FOR HIGH  
EFFICIENCY VTE OR MULTI-STAGE FLASH EVAPORATORS

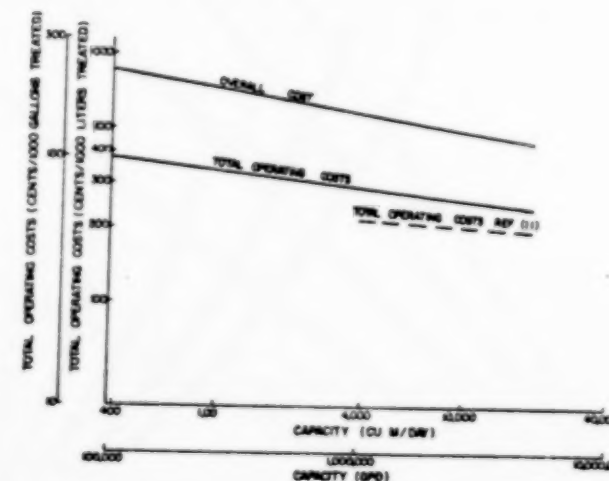


FIGURE 77  
OVERALL AND TOTAL OPERATING COSTS  
FOR VTE AND MULTI-FLASH EVAPORATORS



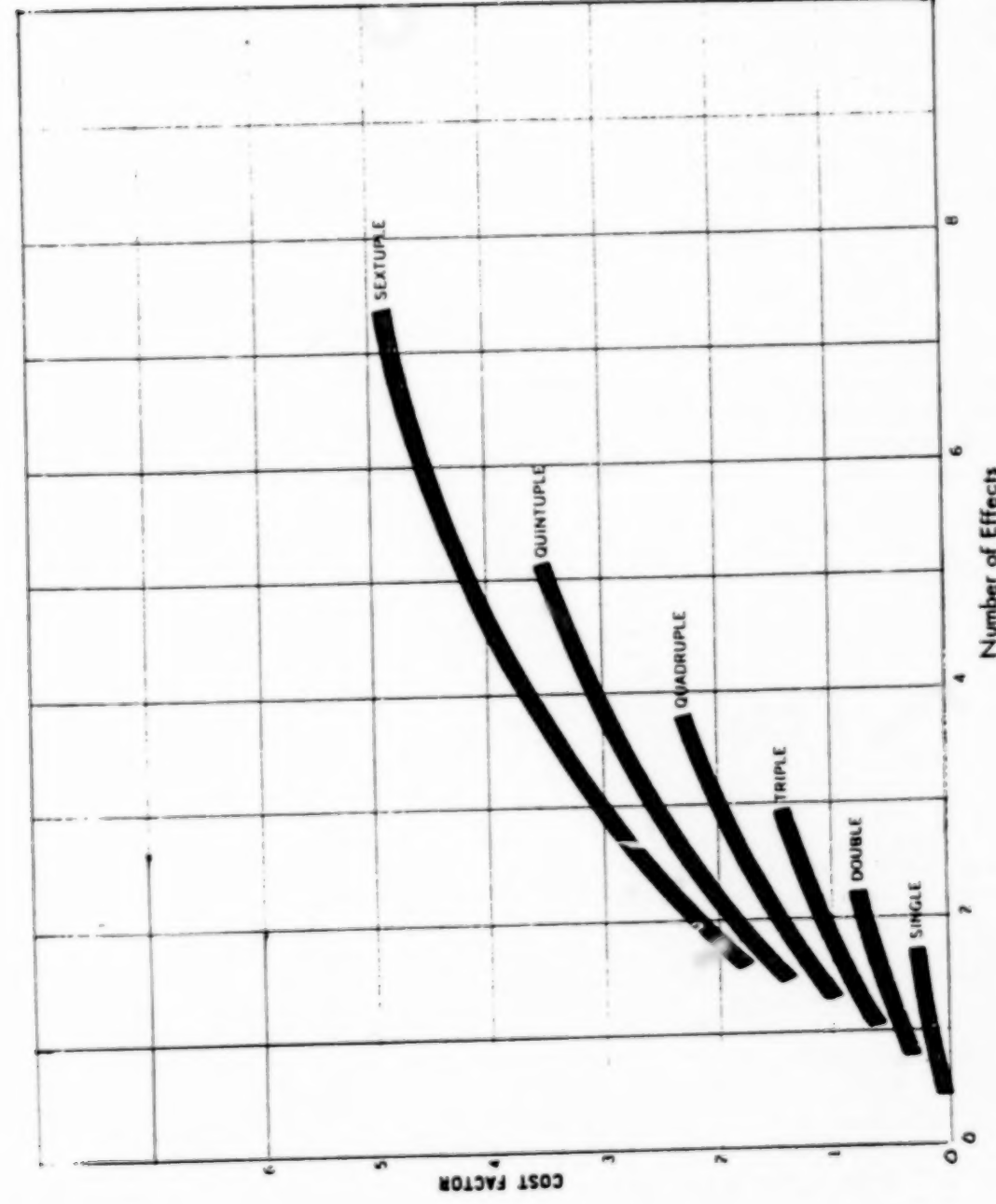


Figure 78. Capital Costs Vs. Effects for Conventional Multi-Effect Evaporators.

# EVAPORATION

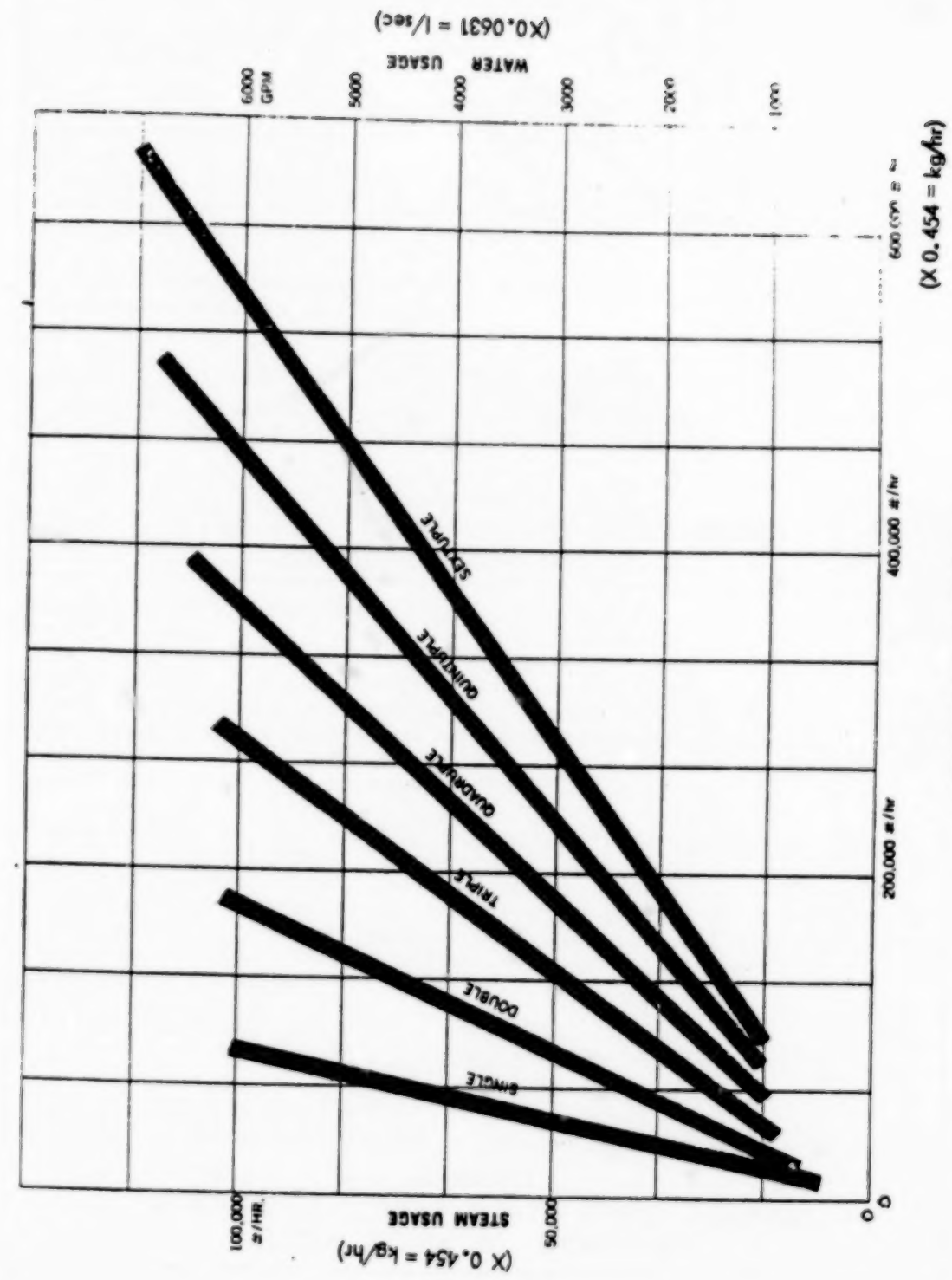


Figure 79. Steam Usage Vs. Effects for Conventional Multi-Effect Evaporators

# EVAPORATION

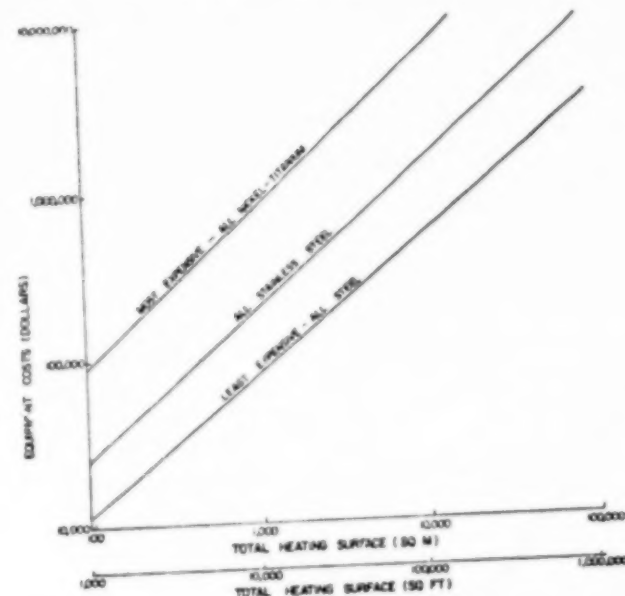


FIGURE 80  
CORRELATIONS OF EQUIPMENT COST WITH  
EVAPORATOR HEATING SURFACE

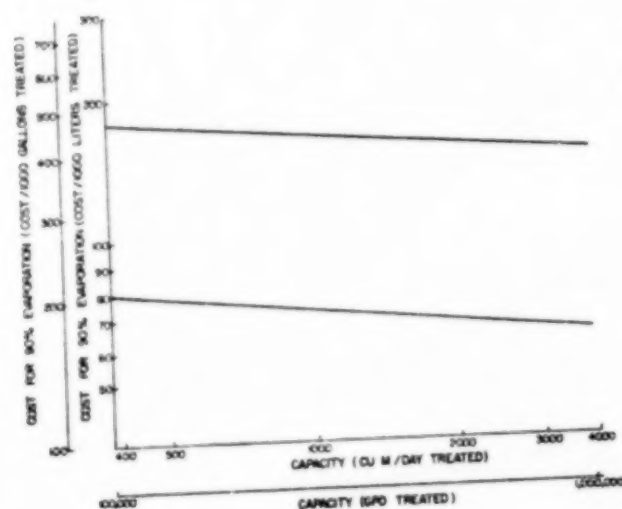


FIGURE 81  
OVERALL COSTS FOR 6-EFFECT EVAPORATOR  
TREATMENT OF WASTE WATER

Volume Treated cu m/day (gal/day)	Total Installed Capital Cost, \$
378 (100,000)	667,000
945 (250,000)	1,530,000
1890 (500,000)	2,800,000
3785 (1,000,000)	5,470,000

Analogous values for stainless steel and other construction material capital costs may be similarly derived.

Operating costs include steam costs and labor and maintenance. Chemical pretreatment costs are usually minimal. Operating costs are summarized below for six-effect evaporators.

Overall costs for all-nickel and stainless steel six-effect evaporators are given in Figure 81.

Volume Treated cu m/day	Volume Treated gal/day	Steam Costs in \$/3785 l (\$/1000 gal)	Labor and Maintenance \$/3785 l (\$/1000 gal)	Total Costs \$/3785 l (\$/1000 gal)
378	100,000	95	91	186
945	250,000	95	80	175
1890	500,000	95	71	166
3785	1,000,000	95	68	163

#### Single-Effect Evaporators

When evaporation loads are small as for final concentrations or minor waste streams, evaporative energy costs are secondary. In these cases, equipment costs and reliability of operation are the controlling considerations. Various designs are available for handling crystallizing solids or slurries and design and industrial technology is widely available.

Using Figure 80 and following the same procedures and costs for energy, installation, maintenance and labor as for multieffect evaporators, costs can be developed. Essentially, costs for single-effect evaporators are treated as an extrapolation of the multi-effect cost values. A summary of the costs involved is shown below for single-effect evaporators assuming stainless steel construction.

Treated cu m/day	Treated gal/day	Installed Capital Costs, \$	Capital Writeoff \$/3785 l (\$/1000 gal)	Operating Costs \$/3785 l (\$/1000 gal)	Overall Costs \$/3785 l (\$/1000 gal)
38	10,000	8,000	34	564	598

189	50,000	28,000	24	551	575
379	100,000	45,000	19	545	564
945	250,000	80,000	14	539	553
1890	500,000	146,000	12	536	548
3785	1,000,000	267,000	11	533	544

Basis:

cu m/day	Treated gal/day	Installation Costs		Labor Costs	
		Percent of equipment capital	\$/3785 l	\$/1000 gal	
38	10,000	100	30		
189	50,000	100	20		
379	100,000	50	17		
945	250,000	33	10		
1890	500,000	33	8		
3785	1,000,000	33	5		

15 percent Capital writeoff/yr.

4 percent Capital cost/yr for maintenance materials.

90 percent Evaporation.

Steam cost -- \$0.70/1000 lbs or \$0.70/454 kg.

Similar values for all nickel, titanium or tantalum construction are:

Treated Volume cu m/day	Treated Volume gal/day	Installed Capital Costs, \$	Total		
			Capital Writeoff \$/3785 l (\$/1000 gal)	Operating Costs \$/3785 l (\$/1000 gal)	Overall Costs \$/3785 l (\$/1000 gal)
38	10,000	16,000	69	574	643
189	50,000	68,000	58	561	619
378	100,000	133,000	57	555	612
945	250,000	300,000	52	549	601
1890	500,000	532,000	46	545	591
3785	1,000,000	1,060,000	45	542	587

Basis: Same as previously shown except 33 percent of capital costs are used for installation estimates for all capacities.

These figures show that single-effect evaporation costs are largely for steam, with capital costs being only a small fraction of the overall cost. All nickel, titanium, tantalum or other high cost materials of construction are often needed and can be economically used.

The high overall costs per liter treated also indicate that single-stage evaporators are restricted to small capacities. For example, at the 3785 cm/day (1,000,000 gal/day) capacity, yearly overall cost for stainless steel equipment is \$1,910,000. Comparable multi-effect and VTE costs are \$583,000 to \$1,400,000 yearly. Obviously the higher efficiency units would be used

whenever possible. At the 379 cu m/day (100,000 gal/day) level, comparable costs are \$198,000/yr for single-effect, \$72,200/yr for six-effect, and \$78,500/yr for 14-effect. For this case, there is still approximately \$120,000/yr savings in going to multi-effect evaporators. Single-effect evaporators would normally be used in the capacity range of 48 cu m/day (10,000 gal/day).

#### Mechanical Drying Costs

The crystallized, suspended or dissolved solids removed in the previous evaporation section can either be recycled, sold, or disposed of in their concentrated form. In some cases, they may require further treatment. Whenever possible, suspended solids should be dewatered by centrifuging or filtration. These relatively low cost treatments may be all that is needed, or reduction to full dryness may be required. When full dryness is required, the filter cakes, centrifuged solids, and concentrated solids may be subjected to conventional thermal drying. Heating may be by gas, oil, or steam. Types of dryers include rotary drum dryers, screw type mechanical dryers, scraped surface tunnel dryers and heated evaporation pans.

Capital costs and labor costs are minimal in comparison to energy costs. Labor and materials are estimated to cost \$0.11 to \$0.33/kg (\$0.10 to \$0.30/ton) of product for small dryers (Reference (71)).

Taking energy costs as \$0.50 per 252,000 kg cal (million BTU) (gas or oil combustion) and an energy utilization efficiency of 50 percent, drying costs are \$1.00/454 kg (1000 lb) of water evaporated.

Drying costs as a function of solids content are given below:

Percent Solids in Feed by weight	Drying Costs, \$/454 kg (\$/10,000 lb)	Drying Costs, \$/3758 l (\$/1000 gal)
90	10	Dry Basis
80	20	Dry Basis
70	30	Dry Basis
60	40	Dry Basis
50	50	420
40	60	500
30	70	580
20	80	600

Aside from the energy costs involved, there are practical drying problems with common dissolved salts such as calcium chloride, potassium chloride, and magnesium chloride. These can be dried but they hold tenaciously to residual water and must be given



special handling techniques including the use of drum flakers or pan evaporators.

#### Deep Well Costs

The capital costs for injection wells vary greatly, from \$40,000 to more than \$1,000,000. The costs depend on factors such as well depth, geology, well hole size, care in drilling, well construction, geographical location, pretreatment requirements, instrumentation and monitoring, corrosion problems, injection pressure, and maintenance. The operating life of such wells is difficult to predict and may be very short due to blockage, contamination of water aquifers, or other reasons.

The principal cost factors in well construction are drilling contractor costs and casing and tubing costs. These two factors comprise approximately two-thirds of the total construction costs. The larger and deeper the hole, the higher the contractor costs will be.

Surface equipment such as pumps, filters, tank, piping, and instrumentation can vary from 50 percent of construction costs to 100 percent or more. Injection pressures above 27 atmospheres (400 psi) require more expensive pumps. Corrosive liquids require more expensive materials in the liquid handling equipment.

The average deep well capital and operating costs determined from a recent comprehensive survey (Reference (77)) are: capital cost -- \$305,000; operating costs -- 30¢/3785 l (1000 gal).

Operating costs for deep well disposal range from 4¢/3785 l (1000 gal) to \$2.20/3785 l (1000 gal). The lower costs are for shallow wells, low injection pressures, minimum pretreatment, relatively low corrosiveness, and a minimum of monitoring and instrumentation. The higher operating costs involve deep wells with high injection pressures, extensive pretreatment, high maintenance costs, extensive monitoring and instrumentation, and corrosion resistant equipment. In any cost calculations involving deep wells, as discussed in Section VII, either a backup well or alternate disposal facility is necessary. This will increase the average capital cost to approximately \$500,000 (for a single-well operation).

Calculating overall costs for deep well disposal at a 1890 cu m/day (500,000 gal/day) rate and using a 15 percent capital amortization yields an overall cost of 73¢/3785 l (1000 gal).

#### Solids Wastes Disposal Costs

The slurries, water soluble solids and water insoluble solids obtained from control and treatment of inorganic chemicals in-

dustry water-borne wastes have to be contained, or disposed of, in a safe and economical manner.

Provided that the solids are insoluble in water, most solid wastes from the inorganic chemicals industry may be land dumped or land-filled. Costs are \$0.22 to \$0.66/kg (\$0.20 to \$0.60/ton) of solids -- for simple dumping or landfilling. Figure 82 gives a breakdown of complete landfilling costs. Large scale operations without cover cost less than \$1.11/kg (\$1.00/ton). If cover is involved for appearance or zoning requirements, the costs may increase to \$1.05 to \$2.20/kg (\$1.50 to \$2.00/ton).

If the evaporation-rainfall situation for the disposal area is favorable (as is the case for much of the southwestern U.S. and some other areas of the country), then landfill in an impervious, lined pan is feasible for soluble solids. Operation costs are similar to those for landfill with no cover, \$0.22 to \$0.66/kg (\$0.20 to \$0.60/ton).

Landfilling of containerized soluble solids in plastic drums or sealed envelopes is practicable but expensive. Blow-molded plastic drums, made from scrap plastic (which is one of the present major problems in solid waste disposal) could be produced for \$11-22/kg (\$10-20/ton) capacity at 227 kg (500 lb) solids per drum and a rough estimate of \$2.50-5.00 cost/drum. A more economical method, particularly for large volumes, would be sealed plastic envelopes, 750 microns (30 mils) thick.

At \$1.10/kg (\$.50/lb) of film, low density polyethylene costs about 10¢ per 0.0929 sq m (1 sq ft). Using the film as trench liner in a 1.8 m (6 ft) deep trench 1.8 m (6 ft) wide, the perimeter (allowing for overlap) would be approximately 7.5 meters (25 feet). At a density of 1.6 gm/cc (100 lb/cu ft) for the solid, costs of plastic sheet/kg would be \$2.00 (\$1.75/ton). With sealing, the plastic envelope cost would be approximately \$2.20/kg (\$2/ton). With landfill costs of \$2.20/kg (\$2/ton) additional, the total landfill disposal costs would be about \$4.40/kg (\$4/ton).

The above figures for soluble disposal using plastic containers, bags or envelopes are only rough estimates. Also, the technology would not be suitable for harmful solids or in situations where leaching contamination is critical.

#### Treatment Costs for Ancillary Water-Borne Wastes

In many plants of this study ancillary wastes such as boiler blowdowns, cooling tower blowdowns, ion exchange regenerants, and contributions from air purification equipment, are either the sole or dominant contributors to water-borne wastes coming from the plant. Rarely is removing these wastes from plant effluent

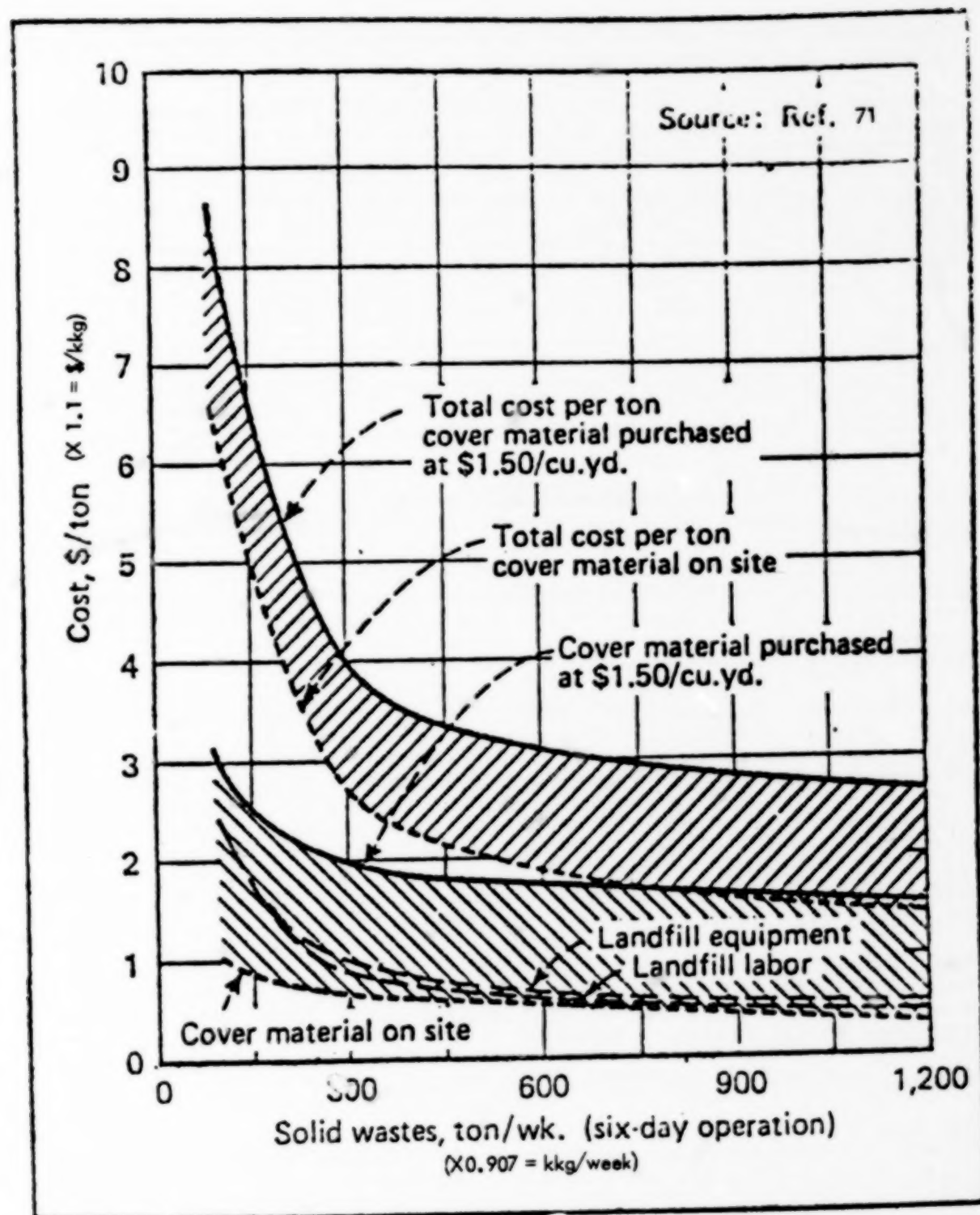


Figure 82. Disposal Costs for Sanitary Landfills

water considered part of the treatment of waste abatement process costs.

#### Air-Borne Waste Abatement Costs

Five chemicals of this study have been selected for specific cost analysis. They are described below.

#### Sulfuric Acid

Reduction of sulfur dioxide in the stack gas of sulfuric acid plants to specified limits is expensive for most existing plants. In each of two plants of this study (113 and 023), over \$2,500,000 has been spent for this purpose alone. As regulations tighten, other plants will have to be modified similarly. The nature of these modifications should be determined by the overall costs and performance of the sulfur dioxide unit considered.

If a sulfuric acid producer does not choose to follow the path of scrubbing sulfur dioxide from the stack gases, it will undoubtedly be more profitable to recycle sulfur dioxide which should have a recovered sales value of approximately \$50/kkg (\$45/ton) and eliminate the expense of sodium hydroxide or other chemicals.

Both add-on double adsorption systems and other processes which have no water-borne wastes exist. New plants all use the double adsorption processes.

#### Calcium Oxide and Calcium Hydroxide

The manufacturing process for calcium oxide and calcium hydroxide has no waste water. The only contribution is from stack scrubbers which collect the lime dust in water.

Current practice is to settle out solids from the scrubber water in ponds and possibly neutralize this effluent before discharge to surface water. Plant 057 currently follows this general type of procedure and plans to install a cyclone recovery and calcining unit on the waste stream at a cost of \$750,000. Cost of installation will be covered by product value obtained. This will remove almost 100 percent of the suspended solids. Some dissolved solids remain. Calcium oxide is soluble to the extent of about 1000 mg/l. The water may be recycled for closed loop scrubbing.

A second approach, which escapes water-borne waste and waste recovery problems, is dry bag collection. The exemplary plant of this study has no water effluent and uses dry bag collection systems. Installation cost was \$675,000 with annual operating costs of \$37,500.



### Calcium Carbide

There is no water-borne process waste from the calcium carbide manufacturing process. The only contributions are ancillary wastes -- cooling tower blowdowns, ion exchange regenerants and gas stream scrubblings.

For water scrubbers, the water effluent may be isolated, suspended solids removed by ponding or chemical treatment, alkalinity neutralized and a closed loop recycle instituted to avoid dissolved solids discharge. Capital costs for a large plant adjusted to 1973 prices are approximately \$750,000 for the scrubber system, \$112,000 for improvements, plus a thickener and settling ponds that will bring the total cost up to \$1,000,000. Recycle is possible but would require equipment modification. Therefore, over \$1,000,000 investment is needed to water-scrub without waterborne waste with both capital and operating costs being losses.

In contrast, one plant of this study uses dry bag collection techniques throughout. Collection and reuse of 10 percent of the raw materials from these dust collectors makes installation profitable, and there are no water-borne wastes involved.

### Chlorine

In contrast to the dusts from the first three processes discussed, chlorine is a reactive and noxious gas. It is soluble in water and forms hypochlorites with water or basic materials present such as sodium hydroxide or calcium hydroxide.

The hypochlorites are bleaches and may be sold. They are also reactive and can be used in the treatment of other chemical wastes such as cyanides. This is done in plant 096. Sodium hypochlorite may also be catalytically decomposed and reused. Discharge must be avoided to attain the effluent reduction possible through the application of the best available technology economically achievable. Removal later from the waste stream will be expensive.

Another method for direct utilization of tail gas chlorine is direct burning with hydrogen to produce hydrochloric acid. Plant 057 is planning this approach at an estimated capital investment of \$430,000. Return on investment looks good from the standpoint of product value and decreased sodium hydroxide usage.

### Aluminum Chloride

The aluminum chloride process has no water-borne wastes, but condenser gas scrubbing removes residual chlorine gas and entrained aluminum chloride fumes. Two exemplary plants (152 and 125) of this study avoid any water-borne wastes as discussed in

Section VII. Costs for a generalized treatment process are shown below to illustrate the dollar values involved. For a discharge of 4.5 kg (10 pounds) of aluminum chloride and 2.25 kg (5 lb) of chlorine per 0.907 kkg (ton) of product in a 18 kkg/day (20 ton/day) plant, treatment costs are developed below for neutralization with sodium hydroxide. Sodium hydroxide costs are estimated to be \$70,000/yr. Also, 195 kg/day (430 lb) of sodium chloride and 53 kg/day (117 lb) of aluminum hydroxide are formed. The volume of neutralized solution is approximately 9461/ day (250 gal/day). Installed cost for a 379/1 (1000 gal) neutralizing, settling and hypochlorite decomposition system plus a small recirculating single-effect concentrator and crystallization system would be approximately \$25,000. Operating costs including steam, electricity, disposal of solid wastes, labor and maintenance, and chemical costs would be approximately \$12,000/yr. Overall costs of capital writeoff plus operating costs would be approximately \$16,000/yr or slightly more than \$2.20/kg (\$2/ton) of product.

### Boiler Blowdowns, Cooling Tower Blowdowns, and Ion-Exchange Regenerants Treatment Systems and Their Costs

Present water treatment facilities in existing plants are usually not designed for zero discharge of water-borne wastes, nor are they designed for complete closed cycle operation. The generalized water treatment facilities given in Figure 63 earlier in this section provide three treatment techniques for removing dissolved solids from makeup and recycle water--demineralization, reverse osmosis and evaporation. It is assumed from the overall treatment model given in Figure 62 (of which Figure 63 is a detailed portion) that suspended solids and toxic materials have already been removed. Figure 83 gives the dissolved solids concentration range over which each type of treatment technique is economically feasible. Costs for different flow rates and dissolved solids contents are given in Table 77. This table shows that if all the incoming and recycle water and blowdowns are less than 1000 mg/l total dissolved solids then demineralizations can be used economically from 1000 mg/l to 3500 mg/l. Specialty demineralization systems are favorable, if available. Most blowdowns are in the 750 mg/l to 3500 mg/l range. Regenerants disposal adds to the overall demineralization costs. With these costs added, the specialty demineralization and reverse osmosis plus evaporation treatment costs are nearly equal in the 1000 mg/l to 3500 mg/l range. If any of the streams coming into the treatment area have greater than 3500 mg/l total dissolved solids, then reverse osmosis and/or evaporation are usually the only treatment approaches.

A model plant example is shown in Table 78 to illustrate needed equipment and costs for treatment.



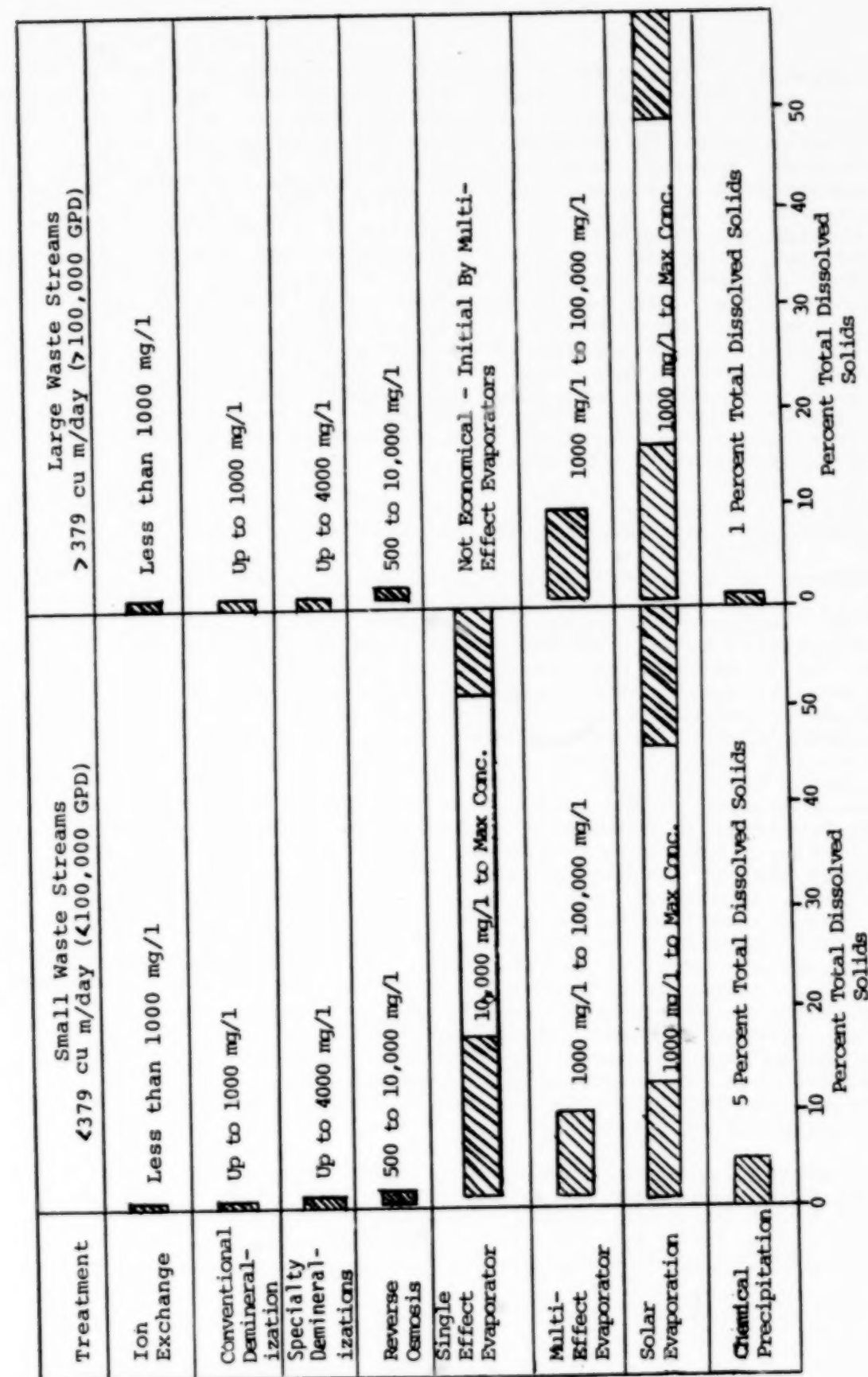


Figure 83. Treatment Applicability to Dissolved Solids Range in Waste Streams.

TABLE 77 Cost Estimates for Different Treatment

Flow cu m/d (GPD)	Demineralization Costs, \$/day	Reverse Osmosis + Evaporation Costs, \$/day
<u>100 mg/liter Total Dissolved Solids</u>		
<u>Conventional Fixed-Bed</u>		
38(10,000)	4	20
379(100,000)	31	142
3785(1,000,000)	220	1005
37850(10,000,000)	2000	6000
<u>1000 mg/liter Total Dissolved Solids</u>		
	<u>Conventional Fixed-Bed</u>	<u>Specialty Systems</u>
38(10,000)	13	7
379(100,000)	121	43
3785(1,000,000)	1120	335
37850(10,000,000)	10,000	~3000
<u>3500 mg/liter Total Dissolved Solids</u>		
	<u>Specialty Systems</u>	
38(10,000)	12	20
379(100,000)	96	142
3785(1,000,000)	861	1013
37850(10,000,000)	8000	6275
<u>10,000 mg/liter Total Dissolved Solids</u>		
38(10,000)	Costs are very high. This is above the application level.	20
379(100,000)		154
3785(1,000,000)		1115
37850(10,000,000)		7600

TABLE 78. Model Treatment Plant Calculations  
Design and Cost Basis

Waste Category	cu m/d (GPD)	Total Dissolved Solids, mg/l
Process Water	379(100,000)	10,000
Cooling Tower Blowdown	38(10,000)	1,000
Boiler Blowdowns	19(5,000)	500
Air Pollution Control	38(10,000)	10,000 (Recoverable at \$33/kg or \$30/ton.)
Makeup Water	189(50,000)	300

Equipment Needed	cu m/d (GPD)	Capital Cost, \$
Demineralizer	379(100,000)	60,000
Reverse Osmosis Unit	379(100,000)	80,000
Multi-Effect Evaporator	94(25,000)	60,000
2-Single-Effect Evaporators	38(10,000)	32,000
Rotary Drum Filter	--	25,000
Centrifuge	--	25,000
		Total \$282,000

Waste Treated	Overall Costs/Day
Process Water	\$ 142
Cooling Tower Blowdown	\$ 45
Boiler Blowdown	\$ 45
Make-Up Water	\$ 45
Air Pollution Control	(\$ 100 credit)
Net Cost	\$ 85 or \$30,000/yr.

In addition to the cost of treating the waste streams, approximately 36-45 kkg (40-50 ton) per day of solids must be disposed of. Disposal costs for these could range from \$1.10 to \$11.00 /kkg (\$1 to \$10/ton). A centralized treatment system as described gives not only zero water-borne waste but also supplies all the demineralized water needed for boilers, operation of cooling water towers at 95 to 98 percent recycle, and reduces process water wastes. Since the treatment equipment is all highly automated, labor costs are also low.

#### Geographic Influences on Treatment and Control Costs

Treatment and control practices and costs for the inorganic chemicals industry depend largely on plant location.

Ocean dumping may be economically feasible only for plants with easy access to the ocean. Even a difference of being located directly on ocean shores as contrasted to being 80 to 160 km (50 to 100 miles) up a bay or river can change barging costs by a factor of two. Ocean barging for titanium dioxide wastes may be as little as \$5.50 /kkg (\$5/ton) of product for well-suited plants. Costs may rise to \$22-\$44/kkg (\$20 to \$40 /ton) for others requiring more capital expenditures and longer barging distances.

Deep-well disposal may be geologically feasible in some parts of the United States but not in others. Brine well salt producers have traditionally deep-welled their wastes. Any other disposal method would raise the disposal costs significantly. An economically feasible method for disposal of wastes from the Solvay soda ash plants is deep-welling. However, deep-welling must be in accordance with local, State and Federal regulations.

Treatment and disposal situations and costs for eastern and western United States differ widely. Water is scarce in most of the west and, therefore, is worth more for recovery and reuse. Pure water may be worth 5.3¢ to 13.2¢/cu m (20¢ to 50¢/1000 gal).

Another difference between eastern and western U.S. is that the West generally has less rainfall. Except for some coastal and isolated areas, western United States has a positive evaporation-rainfall differential. This positive differential makes it possible to dispose of water-borne wastes by solar evaporation. Disposal costs as low as 7.9¢/cu m (30¢/1000 gal) were given earlier in this section. Comparable deep welling costs are 19.3¢/cu m (73¢/1000 gal).

The location, character, and size of the company-owned land around the plant is becoming increasingly important. Many of the older plants in the inorganic chemical industry are built on small plots, surrounded by industrial and residential neighbors. Industries such as hydrofluoric acid, titanium dioxide and sodium

dichromate have heavy solid waste loads but often limited storage capacity. Even where wastes can be successfully disposed of outside the premises, costs are higher than for plant site storage.

## SECTION IX

### EFFLUENT REDUCTION ATTAINABLE THROUGH THE APPLICATION OF THE BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE

The effluent limitations which must be achieved by July 1, 1977 are based on the degree of effluent reduction attainable through the application of the best practicable control technology currently available. For the inorganic chemical industry, this level of technology was based on the best existing performance by exemplary plants of various sizes, ages and chemical processes within each of the industry's product subcategories.

Best practicable control technology currently available emphasizes treatment facilities at the end of a manufacturing process but also includes the control technology within the process itself when it is considered to be normal practice within an industry. Examples of waste management techniques which were considered normal practice within the inorganic chemicals industry are:

- a. manufacturing process controls
- b. recycle and alternative uses of water
- c. recovery and/or reuse of waste water constituents.

Consideration was also given to:

- a. The total cost of application of technology in relation to the effluent reduction benefits to be achieved from such application;
- b. The size and age of equipment and facilities involved;
- c. The process employed;
- d. The engineering aspects of the application of various types of control techniques;
- e. Process changes;
- f. Non-water quality environmental impact (including energy requirements).

The following is a discussion of the best practicable treatment methods currently available for each of the chemical subcategories, and the effluent limitations on the significant pollutant parameters in their effluents.



#### EFFLUENT REDUCTION ATTAINABLE USING BEST PRACTICABLE TECHNOLOGY CURRENTLY AVAILABLE

Based upon the information contained in Sections III through VIII of this report, the following determinations were made on the degree of effluent reduction attainable by the application of the best practicable control technology currently available in the various subcategories of the inorganic chemicals industry.

##### General Water Guidelines

Process water is defined as any water directly contacting the reactants, intermediates, waste products, or end-products of a manufacturing process including contact cooling water. Not included in the guidelines are noncontact cooling water or ancillary waste streams resulting from steam and water supply. All values of guidelines and limitations presented below are expressed as kg of pollutant/kg of product (lb/ton). While concentrations and flow are cited as the basis on which the guidelines were developed, the effluent limitations describe the allowable quantities of pollutants which may be discharged per unit of production. No limitations are established for either pollutant concentration or process waste water flow. The daily maximum limitation is double the thirty day average. Extensive, long-term data is not available for each of the 22 chemical subcategories. It was necessary, therefore, to rely on data from other segments of the inorganic chemicals industry, as well as data from other industrial categories. Based on this information and using good engineering judgement on the performance reliability of recommended treatment systems, a factor of two appears reasonable.

##### Aluminum Chloride

The process used for the manufacture of anhydrous aluminum chloride uses no water except in cases where a scrubber is employed to eliminate or reduce the discharge of unreacted chlorine gas. There are essentially three different grades of anhydrous aluminum chloride product made using the process of reacting chlorine gas with molten aluminum. The grey product is aluminum-rich, the white product is made from stoichiometric quantities of aluminum and chlorine, and the yellow product is chlorine-rich. The grey and white product manufacture releases little or no chlorine from the reactor and, therefore, dry collection methods can be employed to minimize air pollution. The manufacture of yellow product requires wet scrubbing to trap the excess chlorine gas.

An exemplary aluminum chloride plant uses a wet scrubber to produce a 28 percent aluminum chloride solution as a product for sale and has no water discharge. In cases where wet scrubbing is required and a favorable market for aluminum chloride solutions

does not exist, the scrubber effluent may be treated to precipitate the aluminum salts from solution. The supernatant may then be recycled to the scrubber. Since the volume of water discharged from the scrubber system in plant 125 is only 2720 l/day (720 gal/day), another treatment approach consists of concentrating the scrubbing water with respect to aluminum chloride by recycling and then evaporating to dryness to recover additional product.

The effluent limitations guidelines for aluminum chloride plants based on best practicable technology currently available require no discharge of process waste water pollutants to navigable waters.

##### Aluminum Sulfate

Aluminum sulfate is made by digesting bauxite ore or aluminum clays in sulfuric acid. The wastes emanating from this process consist of insolubles such as iron and silicon oxides. These wastes are removed during settling and filtration of the product alum solution and also during washdown of tanks. In two exemplary plants (049 and 063), the waste muds are ponded to settle the solids and the clear water is recycled to the process. No process waste water pollutants are discharged. Costs for the entire aluminum sulfate industry to achieve this level of pollution control average \$0.90/ton of product, which is approximately 1.5 percent of the list price of aluminum sulfate.

While it is recognized that the raw waste load generated by the manufacture of aluminum sulfate increases when aluminum clays or other impure raw materials are used as the source of aluminum, the production process is the same as for bauxite ore. Therefore, the use of raw materials other than bauxite ore does not preclude adoption of the best practicable technology currently available. One plant using clay as its raw material is able to totally recycle its process water.

Because of the negative water balance associated with aluminum sulfate production, the pond supernatant may be totally recycled with no discharge of process waste water pollutants. Muds and other impurities settle out and allow the supernatant to be reused without a build-up of contaminants. A discharge allowance is provided to permit the discharge of rainwater in excess of evaporation. This water must be treated to a 25 mg/l suspended solids concentration on the average and be within the pH range of 6.0 to 9.0. An untreated discharge is allowed in the event of a catastrophic rainfall in excess of the maximum 24-hour, 10-year rainfall event.

The effluent limitations guidelines for aluminum sulfate plants based on best practicable technology currently available require

no discharge of process waste water pollutants to navigable waters.

No discharge of process waste water pollutants to navigable waters is also the effluent limitation for plants producing iron-free alum. The production of iron-free alum requires pure raw metals, that is, iron-free sulfuric acid and iron-free hydrated alumina. The refining of the bauxite to produce the iron-free hydrated alumina yields wastes that must be segregated from the alum production process waters. The refining of bauxite to alumina is included in the nonferrous metal manufacturing point source category. Effluent guidelines for this refining process are presented therein.

#### Calcium Carbide

The data cited from plant 190 using an open furnace shows that the only manufacturing wastes involved are dusts emerging in tail gases from the furnaces. These are collected by dry bag filtration methods and are reused in the process or disposed of as solid wastes by landfilling. Dry bag collection of solid waste constitutes the best practicable control technology currently available. Because the segment of the calcium carbide industry covered herein is currently using this technology, no additional costs are required for treatment. Because plants manufacturing calcium carbide in covered furnaces typically recover the waste carbon monoxide, dry bag collection may be not universally applicable. Wet scrubbers are typically used to remove impurities from this gaseous stream. Hence, plants using covered furnaces are considered separately and will be included in a forthcoming study.

The effluent limitations guidelines for calcium carbide plants using open furnaces based on best practicable technology currently available require no discharge of process waste water pollutants to navigable waters.

#### Calcium Chloride

Calcium chloride is produced by extraction from natural brine and as a by-product of soda ash manufacture by the Solvay Process. The guidelines presented herein apply only to the brine extraction process.

The process wastes are weak brine solutions, which emanate from the blowdown of various brine purification steps and from several evaporation steps used in the process. The best practicable treatment technology is to pass the waste brine streams through ponds to settle suspended solids and adjust pH. Final ponding is used to remove additional suspended solids before discharge. The process water discharge flow averages 330 l/kg of product (79 gal/ton), and contains suspended solids but no harmful metals.

The limitations are based on the performance of a well-designed and operated settling basin which will reduce the concentration of suspended solids to 25 mg/l. While it is recognized that significant quantities of dissolved solids may be present in the effluent, it was concluded that removal of these pollutants requires advanced treatment and expense beyond the definition of best practicable technology.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after application of the best practicable control technology currently available by calcium chloride plants using the brine extraction process:

TSS	0.0082 kg/kg (0.0164 lb/ton)
pH	within the range 6.0 to 9.0

#### Calcium Oxide and Calcium Hydroxide

The manufacture of calcium oxide by the calcination of limestone is a dry process and uses only noncontact cooling water, and, in some cases, scrubber water. Plant 007 uses dry bag dust collectors and, therefore, discharges no process water. The use of dry bag collection methods is not contingent on the use of specific fuels for the calcination kilns nor is it geographically dependent. In plants with wet scrubbing systems already installed, the scrubbing solution may be reused in the process, or used to produce a low-grade product. One lime plant using wet scrubbers is able to completely recycle the scrubbing solution. Solids may be removed in settling vessels or ponds. For plants using ponds for treatment prior to reuse, a provision has been established to allow a discharge from impoundments in areas where rainfall exceeds evaporation. This discharge must be within the pH range of 6.0 to 9.0 and contain, on the average, a suspended solids concentration not to exceed 25 mg/l. In the event of a catastrophic rainfall exceeding the maximum 10-year, 24-hour event, an untreated discharge is allowed.

Plants using dry baghouses will not have to spend additional money to achieve the effluent reduction attainable by the application of best practicable technology currently available. Plants with wet scrubbers may have to invest up to an average of \$1.28/ton of product.

The effluent limitations guidelines for calcium oxide and calcium hydroxide plants based on best practicable technology currently available require no discharge of process waste water pollutants to navigable waters.

#### Chlorine and Potassium or Sodium Hydroxide

(a) Diaphragm cell process



The diaphragm cell process for the manufacture of chlorine and caustic soda or caustic potash usually have the following raw wastes emanating from the process:

- a. a solution of sodium hypochlorite and sodium bicarbonate from the scrubbing of chlorine tail gases (about 7.5 kg of dissolved solids/kg of chlorine produced).
- b. chlorinated organics from the liquifaction of chlorine gas (about 0.7 kg/kg of chlorine produced)
- c. brine wastes from the brine purification system (about 12.2 kg of dissolved solids /kg of chlorine produced)
- d. spent sulfuric acid from the chlorine drying process (about 4.2 kg/kg of chlorine produced)
- e. weak caustic and brine solution from the caustic evaporators using barometric condensers (about 9.5 kg of dissolved solids/kg of chlorine produced)
- f. weak caustic and brine solution from the caustic filter washdown (about 37.5/kg of dissolved solids/ kg of chlorine produced).

At plant 157, the tail gas scrubber wastes are presently discharged. However, the installation of a chlorine burning hydrochloric acid plant will eliminate the scrubber wastes. This addition is practicable, as substantiated by plant 157's plans for installation in the near future. The chlorinated organics are disposed of by incineration. The brine wastes from brine purification are ponded to settle out suspended solids and the brine liquor is recycled to brine make-up. The spent sulfuric acid at this plant is utilized elsewhere in the complex or may be sent to a spent sulfuric acid plant for regeneration. Some plants presently use this acid to partially neutralize caustic wastes in the plant which aides in controlling the effluent pH. The weak caustic/brine solution from the caustic evaporators can be eliminated by replacing the barometric condensers with noncontact surface condensers or by recycling the discharge from the barometric condenser back to brine make-up. The weak caustic/brine solution from the caustic filters is presently pH adjusted and discharged. Diaphragm cell chlorine plants will need to invest approximately \$0.30/ton of chlorine produced to implement best practicable technology currently available.

Lead is sometimes present in the effluent as a result of cracks around protective resin seals which encase underlying lead mountings. Currently one-third of the industry is using anodes which eliminate the lead discharge. Industry representatives state that another one-third are seriously considering conversion. The lead limitation is the average value discharged from three plants which have not converted to lead-free anodes. The suspended solids limitation is based on a well-operated sedimentation vessel or pond designed to treat suspended solids to a 25 mg/l concentration.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after application of the best practicable control technology currently available by diaphragm cell chlor-alkali plants:

TSS	0.32 kg/kg (0.64 lb/ton)
Lead	0.0025 kg/kg (0.005 lb/ton) of chlorine
pH	within the range 6.0 to 9.0

#### (b) Mercury cell process

The mercury cell process for the manufacture of chlorine and caustic soda or caustic potash usually has similar wastes to the diaphragm cell process. The major exception is the loss of mercury from the process. Exemplary plants 144, 098 and 130 have excellent mercury control systems to minimize the incorporation of mercury into discharge streams. These controls consist of curbing the cell area to retain mercury lost in spills or leaks, collecting all mercury before ponding and discharge and/or recycling mercury-containing waste water back to the cells for reuse after treatment to remove any impurities. These plants have continuous mercury monitors on streams possibly contaminated that are meant for ponding to settle suspended solids before discharge. The mercury recommendation is twice the discharge performance achieved by the three plants studied, whose discharges per ton of chlorine are very similar. The mercury limitation represents the quantity of mercury discharged from the mercury treatment system. Residual mercury may be present in other portions of the plant and may contribute to the total mercury discharge. Residual mercury levels are difficult to quantify on a production basis and are, therefore, not the subject of the limitations presented below. Costs for the industry to achieve best practicable technology currently available are estimated to be \$2.74/ton of chlorine produced.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after application of the best practicable control technology currently available by mercury cell chlor-alkali plants:

TSS	0.32 kg/kg (0.65 lb/ton) of chlorine
Mercury	0.00014 kg/kg (0.00028 lb/ton) of chlorine
pH	within the range 6.0 to 9.0

#### Hydrochloric Acid

The manufacture of hydrochloric acid by the chlorine burning process comprises a minor part of total U.S. production. All of the chlorine burning facilities are located within chlor-alkali complexes. Plant 121 is one such facility. The only waste generated from this process consists of weak hydrochloric acid, which is generated only during startup of the operation. No



waste emanates from the process during normal operation. The startup weak acid waste is normally neutralized with sodium hydroxide which yields dissolved solids (sodium chloride) amounting to about 0.5 kg/kg (1 lb/ton) of product acid. The weak brine startup waste from the hydrochloric acid plant may be utilized in the brine make-up operation at the chlor-alkali portion of the complex, reused in acid manufacture.

Any leaks and spills must be contained and collected. If adequately segregated from other waste streams, the spills and leaks may be reused or sold. Good housekeeping, operation and maintenance will minimize or eliminate leaks and spills.

The effluent limitations guidelines for chlorine-burning hydrochloric acid plants based on best practicable technology currently available require no discharge of process waste water pollutants to navigable waters.

#### Hydrofluoric Acid

The manufacture of hydrofluoric acid by the reaction of fluospar (about 97 percent calcium fluoride) with sulfuric acid generates about 3.1-3.6 kkg (3.5 - 4.0 tons) of solid waste/kg of product acid. All wastes from the process may be water slurried to settling ponds, and the clear liquid recycled. All process water can be segregated from noncontact cooling water. At least one plant in the industry uses this recycle technology to eliminate its process waste water discharge.

All leaks and spills must be contained and may be recycled, sold or pumped to the settling pond for treatment prior to reuse. Good housekeeping, operation, and maintenance will minimize or eliminate leaks and spills. A discharge is permitted from the impoundment if rainfall exceeds evaporation, or in the event of a catastrophic rainfall in excess of the maximum 24-hour, 10-year event. Except from discharges as a result of a catastrophic rainfall, the thirty-day average concentration of any effluent must not exceed 25 mg/l suspended solids and 15 mg/l fluoride. The pH must be within the range 6.0 to 9.0.

The effluent limitations guidelines for hydrofluoric acid plants based on best practicable technology currently available require no discharge of process waste water pollutants to navigable waters.

#### Hydrogen Peroxide

##### (a) Organic process

The organic process for the manufacture of hydrogen peroxide at plant 069 generates a waste stream containing 0.17-0.35 kg/kg (0.34-0.70 lb/ton) of organics. The treatment methods currently

used at this plant include an 80 percent reduction of hydrogen peroxide to water and oxygen, a recovery system which recovers 60-70 percent of lost organics, and tank diking and process curbing to retain waste spills. The process water use in this facility is 16,000 l/kg of product (3,800 gal/ton) and contains, after treatment, suspended solids and organic matter, but no harmful metals. The guidelines are based on the treatment systems used at plant 069 and the actual performance of these operations. The cost to implement these technologies is estimated to be \$1.00/ton of product.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after application of the best practicable control technology currently available by organic process hydrogen peroxide plants:

TSS	0.40 kg/kg (0.80 lb/ton)
TOC	0.22 kg/kg (0.44 lb/ton)
pH	within the range 6.0 to 9.0

##### (b) Electrolytic process

There is only one plant in the U.S. that makes hydrogen peroxide by the electrolytic process. Plant 100 recovers all of the solids present in the process wastes and uses an ion exchange system to remove 98 percent of the cyanides present in the waste stream before discharge. The ion exchange regenerant is pH controlled prior to discharge. The effluent limitations are based on the performance of treatment systems employed at plant 100. Suspended solids are discharged in concentrations less than 25 mg/l and the oxidizable cyanide concentration averages 2 mg/l.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after application of the best practicable control technology currently available by electrolytic process hydrogen peroxide plants:

TSS	0.0025 kg/kg (0.005 lb/ton)
Cyanide	0.0002 kg/kg (0.0004 lb/ton)
pH	within the range 6.0 to 9.0

#### Nitric Acid

Commercial grade nitric acid (up to 70 percent concentration) is made by the oxidation of ammonia. At plant 114, all process waters are recycled with no discharge of process waste water pollutants. Of the 30,280 cu m (8 million gal) of water/day used for cooling, about 95 percent is recycled. An additional 757 cu m/day (0.02 mgd) are used to make steam and 75 percent of this quantity is recycled. About 87 cu m (23,000 gal)/day of steam condensate is used for acid make-up water. The discharge from the plant consists of noncontact cooling water which contains

blowdowns from boilers, cooling towers and water treatment with a total waste load amounting to about 2 kg/kg (4 lb/ton) of product produced.

The best practicable treatment technology available for commercial grade nitric acid plants is the recycle of all process waters and the segregation of process waters from cooling water as demonstrated in plant 114. Volumes of waste water as a result of leaks and spills may be minimized or eliminated by good housekeeping, operation and equipment maintenance. These waste waters should be collected and may be recycled with the weak acid streams from condensers or may be sold as a weak acid product. It is estimated that \$0.22/ton of product is required to implement these technologies.

The effluent limitations guidelines for plants producing nitric acid up to 70 percent concentration based on best practicable technology currently available require no discharge of process waste water pollutants to navigable waters.

#### Potassium Metal

Plant 045 produces most of the potassium metal manufactured in the U.S. by a completely dry process. No water is used. Therefore, the effluent limitations guidelines based on best practicable technology currently available require no discharge of process waste water pollutants to navigable waters.

#### Potassium Dichromate

The process for the production of potassium dichromate involves the reaction of potassium chloride with sodium dichromate. At plant 002, all process water is recycled and sodium chloride (400 kg/kg of product) is removed as a solid waste. The only water-borne waste source is contamination of cooling water by hexavalent chromium in a barometric condenser presently in use on the product crystallizer. The plant has plans to replace the barometric condenser with a noncontact heat exchanger which will eliminate cooling water contamination. Best practicable technology currently available requires total recycle of process waste waters. The waste liquor from the salt concentrator may be recycled to the reaction mix tank. Chromium discharges may be eliminated by installing noncontact heat exchangers. Costs to implement these technologies are estimated to be \$4.65/ton of product. This is approximately one percent of the list price of potassium dichromate.

The effluent limitations guidelines for potassium dichromate plants based on best practicable technology currently available require no discharge of process waste water pollutants to navigable waters.

#### Potassium Sulfate

All of the potassium sulfate manufacturers in the U.S. are located in the arid southwest near deposits of langbeinite ore ( $K_2SO_4 \cdot 2MgSO_4$ ). The reaction of this ore with a potassium chloride solution and the subsequent crystallization and separation of potassium sulfate from magnesium chloride brine constitutes the process for the production of potassium sulfate. A large amount (about 2000 kg/kg of product) of magnesium chloride brine is a co-product of this process. Plant 118 sells most of this brine when the sodium content of the ore is low. It ponds the brine for evaporation when it cannot be sold. Evaporation ponds in this area of the country are feasible. The cost of water is a problem and most of the liquor in the brine is recycled back to the process for reuse before the magnesium chloride is sold or dumped. Other insoluble wastes from the process muds amount to about 15 kg/kg of product, and they are landfilled. Because of the geographical dependence of plants manufacturing potassium sulfate to the arid southwest evaporation ponds are considered to be the best practicable technology currently available.

The effluent limitations guidelines for potassium sulfate plants based on best practicable technology currently available require no discharge of process waste water pollutants to navigable waters.

#### Sodium Bicarbonate

Sodium bicarbonate is manufactured by the carbonation of a sodium carbonate solution. Most plants are located in or near complexes manufacturing soda ash by the Solvay Process. There is one isolated facility which uses mined soda ash as a raw material. Plant 166 is located within a Solvay Process complex. The major wastes from this process are about 10 kg of undissolved sodium bicarbonate/kg of product and an average of about 38 kg of dissolved sodium bicarbonate/kg of product. Some of the undissolved sodium bicarbonate is reusable and it is redissolved and recycled to the process. The remainder is landfilled along with sand from the filters and other non-process solid waste. The weak slurry thickener overflow, which constitutes their present source of waste, may be used as a source of liquid for the product dryer scrubber. Recycling this liquid to concentrate it with respect to sodium carbonate will enable it to be reused in the process. These process changes will eliminate the discharge of process waste waters. One plant plans to incorporate this technology into its manufacturing process.

Costs for implementation of best practicable technology currently available are expected to be offset by recovered product values.



The effluent limitations guidelines for sodium bicarbonate plants based on best practicable technology currently available require no discharge of process waste water pollutants to navigable waters.

#### Sodium Carbonate

The Solvay Process for the manufacture of sodium carbonate (soda ash) involves the reaction of sodium chloride brine, ammonia and carbon dioxide to yield crude soda ash. The ammonia is recovered from the process by reacting the spent brine solution with lime followed by distillation. This process produces about 1500 kg of dissolved solids waste/kg of soda ash manufactured. Calcium chloride comprises the majority of this waste, amounting to about 1050 kg for every kkg of soda ash. Plant 166 recovers about 21 percent of the waste calcium chloride for sale. The total recovery of calcium chloride is not practical because of the limited market. The only treatment used at this plant is a settling pond to reduce the concentration of suspended solids in the effluent. Therefore the effluent limitations guidelines are not based on by-product recovery, but upon the water flow necessary to maintain the total calcium chloride by-product formed in the process at a 10 percent concentration at discharge 900 l/kg of soda ash (1,650 gal/ton). Suspended solids but no harmful metals may also be present. Large quantities of dissolved solids, primarily chlorides, are generally present in the effluent. Considering the available treatment technologies to remove chlorides and their associated costs, it was concluded that, in this case, dissolved solids removal is beyond the scope of best practicable technology currently available.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after application of the best practicable control technology currently available by sodium carbonate plants using the Solvay Process:

TSS	0.17 kg/kg (0.34 lb/ton)
pH	within the range 6.0 to 9.0

#### Sodium Metal

The process for the manufacture of sodium metal, commonly called the Downs Cell Process, is essentially dry. However, water-borne wastes are generated during cleanout and washdown of cells when the electrolyte is replenished, from scrubbing chlorine tail gases and from drying the chlorine with sulfuric acid. At plant 096, the spent drying acid is not discharged but used elsewhere in the works complex. The wastes from cell wash-downs, runoff water and residual chlorine-containing water from the tail gas scrubber are ponded to settle suspended solids and then discharged. At plants where the utilization of the spent drying acid and calcium hypochlorite solution is not possible, the spent

acid may be recovered or sold to a "decomp" sulfuric acid plant and the calcium hypochlorite solution be recovered and marketed as a bleach product. The limitations are based on the discharge volume of process water other than barometric condensers which contributes only small quantities of TSS. Treatment of the process water in well-designed settling basins to a 25 mg/l concentration is considered to be best practicable technology currently available.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after application of the best practicable control technology currently available by sodium metal manufacture plants:

TSS	0.23 kg/kg (0.46 lb/ton)
pH	within the range 6.0 to 9.0

#### Sodium Chloride

##### (a) Solar evaporation process

Solar salt is produced by the long-term solar evaporation of sea water to precipitate sodium chloride. This process generates a bittern waste solution consisting mainly of sodium, potassium and magnesium salts. Plant 059 reclaims some of the waste salts from the bitterns and stores the rest for future reclamation. Because this impoundment procedure is dependent on the availability of large areas of land for storage ponds, it may not be generally applicable. Until recovery of magnesium and potassium values proves economical, unused bitterns may be returned to the source of the original brine solution provided that no additional pollutants are added.

##### (b) Solution brine-mining process

Sodium chloride manufacture by this process involves pumping water into an underground salt deposit (solution mining) and returning the brine for treatment to remove impurities. Multiple effect evaporators are used to crystallize and collect the pure sodium chloride for sale. At plant 030, the brine sludges from the brine purification step are disposed of by returning them to the mine. Other sources of waste water are the purges from the evaporators, spills and the barometric condenser. All of the concentrated brine wastes are recycled to the process. The current plant effluent is neutral in pH and low in suspended solids. Best practicable technology currently available consists of treating the solid-containing waste streams in a well-designed and operated settling pond.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after application of the best practicable control technology currently



available by solution mining evaporative process sodium chloride plants:

TSS	0.15 kg/kkg (0.30 lb/ton)
pH	within the range 6.0 to 9.0

#### Sodium Dichromate and Sodium Sulfate

These two chemicals are manufactured as co-products by the calcination of a mixture of chrome ore, soda ash and lime followed by water leaching and acidification of the soluble chromates. The sodium sulfate product is crystallized out after acidification. The bulk of the waste originates from the undigested portions of the ore and is mostly solid wastes. Water-borne wastes arising from spills and washdowns contain most of the hexavalent chromium. Treatment at plant 184 consists of containment of spills, leaks and rain water runoff in chromate areas of the plant, followed by treating the chromium-containing waste water with pickle liquor to affect reduction of the chromates and then lagooning to settle suspended solids before discharge. This treatment removes 99 percent of the hexavalent chromium. Dichromate plant 014 uses the more conventional sodium hydrosulfide treatment to reduce the hexavalent chromium. Subsequent lime treatment limits the discharge to the solubility limits of calcium sulfate (2000 mg/l) and about 0.05 mg/l of unreacted hexavalent chromium and a total chromium level of 0.44 mg/l. The effluent limitations are based on chromium treatment to these levels and suspended solids removal in a well-operated settling basin, designed to reduce TSS to a 25 mg/l concentration. Costs to achieve this treatment level are estimated to be \$16/ton of sodium dichromate which is about 4.6 percent of its list price.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after application of the best practicable control technology currently available by sodium dichromate and sodium sulfate coproduct plants:

TSS	0.22 kg/kkg (0.44 lb/ton)
Cr (+6)	0.0009 kg/kkg (0.0018 lb/ton)
Cr (T)	0.0044 kg/kkg (0.0088 lb/ton)
pH	within the range 6.0 to 9.0

#### Sodium Silicate

Sodium silicate is produced by the reaction of soda ash and silica in a furnace to form a sodium silicate glass. The material is sold either as a solid glass product or is pressure dissolved in water and sold as a solution with various ratios of silica to sodium oxide. The water-borne waste generated consists of unreacted silica, sodium hydroxide and sodium silicate from

tank washdowns, product shock cooling with water and scrubber effluent. At plant 072, these wastes are ponded to settle the solids and the clear liquid is partially recycled. Best practicable technology currently available consists of sedimentation and neutralization of the effluent. The suspended solids settle efficiently and the waste water should contain only dissolved sodium sulfate and virtually no sodium silicate.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after application of the best practicable technology currently available by sodium silicate plants:

TSS	0.005 kg/kkg (0.01 lb/ton)
pH	within the range 6.0 to 9.0

#### Sodium Sulfite

Sodium sulfite is manufactured by the reaction of sulfur dioxide with soda ash. The process wastes are mainly sulfides from product purification and sodium sulfite/sodium sulfate solutions from the product dryer ejector, filter washings and vessel cleanouts. Plant 168 is the only sodium sulfite plant currently treating the waste sulfite-containing solutions to oxidize sulfite to sulfate. The efficiency of this aeration treatment is about 94 percent. This treatment reduces the COD to the level required by best practicable technology currently available. An additional filtration treatment is given to the process waste water which removes 98 percent of the suspended solids. This treatment reduces TSS to below 25 mg/l. The limitations are based on the waste stream emanating from the dryer ejector and filter wash operations of this plant at the high end of its range (630 l/kkg or 150 gal/ton).

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after application of the best practicable control technology currently available by sodium sulfite plants:

TSS	0.016 kg/kkg (0.032 lb/ton)
COD	1.7 kg of dichromate ion/kkg
pH	within the range 6.0 to 9.0

#### Sulfuric Acid

Sulfuric acid is manufactured using the sulfur-burning contact process by three different types of plants. These are single absorption plants, double absorption plants and spent acid plants. The guidelines presented herein do not apply to spent acid plants or by-product sulfuric acid production, as in copper smelting operations.

Plant 141 is a single absorption plant and plant 086 is a double absorption plant. The double absorption plant has no process waste and uses only noncontact cooling water. The single absorption plant requires the use of wet scrubbing to minimize air pollution, and the scrubber water is recycled. There is no discharge of process waste water from these plants. A sulfuric acid plant in Finland neutralizes its scrubber water. The salt solution is then concentrated into fertilizer feed. Leaks and spills may be minimized or eliminated by good housekeeping, operation and equipment maintenance. Leaks should be segregated from other waste streams and may be reused in the process or sold as a weak acid solution.

The effluent limitations guidelines for single and double absorption sulfur burning sulfuric acid plants based on best practicable technology currently available require no discharge of process waste water pollutants to navigable waters.

#### Titanium Dioxide

##### a) Chloride process

Chloride process plant 009 uses neutralization, clarification and ponding to settle suspended solids and to precipitate metals. About 93 percent of the cooling water is recycled but there appears to be no practical approach for recycling process water. Deep well disposal is utilized by another company (plant 160). The plant effluent is neutral pH and contains mostly sodium chloride as the dissolved solid.

Best practicable technology currently available consists of lime treatment and sedimentation to reduce the iron concentration to 4 mg/l and the TSS to 25 mg/l. The guidelines are only applicable to discharges resulting from titanium dioxide production. They do not include any wastes resulting from ore beneficiation. In some cases, all titanium tetrachloride is not used to produce titanium dioxide. The guidelines include only those wastes which may be attributed to titanium dioxide production.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after application of the best practicable control technology currently available by titanium dioxide plants using the chloride process:

TSS	2.2 kg/kkg (4.4 lbs/ton)
Iron	0.36 kg/kkg (0.72 lb/ton)
pH	within the range 6.0 to 9.0

##### b) Sulfate process

The high iron content in the ilmenite ore raw material is a major source of the wastes generated by this process. Another major

contributor to the process waste is the large amount of spent sulfuric acid from digestion of the ore. Very little treatment is presently being used and the effluents from these plants are highly acidic and contain high concentrations of suspended and dissolved solids including metal ions. Ocean barging is used by some to dispose of the process waste waters. Plant 122 is presently installing treatment facilities to neutralize and oxidize the process waste to remove acid as calcium sulfate, to reduce the chemical oxygen demand and reduce the concentration of harmful metal ions. Additional settling ponds are planned to reduce the quantities of suspended solids formed during the neutralization treatment. Considerable research is being done to improve treatment technologies for this process. Best practicable technology currently available consists of lime neutralization and settling. This treatment system will remove iron and suspended solids, while coprecipitating other metal ions such as vanadium, chromium, and manganese. The limitations are based on a suspended solids concentration of 50 mg/l and an iron concentration of 4 mg/l. A flow basis of 210,000 l/kkg was used. This flow may be achieved by recycling scrubber water to the process.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after application of the best practicable control technology currently available by sulfate process titanium dioxide plants:

TSS	10.5 kg/kkg (21.0 lb/ton)
Iron	0.84 kg/kkg (1.68 lb/ton)
pH	within the range 6.0 to 9.0



## SECTION X

### EFFLUENT REDUCTION ATTAINABLE THROUGH THE APPLICATION OF THE BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE,

The effluent limitations which must be achieved by July 1, 1983 are based on the degree of effluent reduction attainable through the application of the best available technology economically achievable. For the inorganic chemical industry, this level of technology was based on the best control and treatment technology employed by a point source within the product subcategory, or where it is readily transferable from one industry process to another.

The following factors were taken into consideration in determining the best available technology economically achievable:

- a. the age of equipment and facilities involved;
- b. the process employed;
- c. the engineering aspects of the application of various types of control techniques;
- d. process changes;
- e. cost of achieving the effluent reduction resulting from application of the best available technology economically achievable; and
- f. non-water quality environmental impact (including energy requirements).

In contrast to the best practicable technology currently available, best available technology economically achievable assesses the availability in all cases of in-process controls as well as control or additional treatment techniques employed at the end of a production process. In-process control options available which were considered in establishing these control and treatment technologies include the following:

- a. alternative water uses
- b. water conservation
- c. waste stream segregation
- d. water reuse
- e. cascading water uses
- f. by-product recovery
- g. reuse of waste water constituent
- h. waste treatment
- i. good housekeeping
- j. preventive maintenance
- k. quality control (raw material, product, effluent)
- l. monitoring and alarm systems.



Those plant processes and control technologies which at the pilot plant, semi-works, or other level, have demonstrated both technological performances and economic viability at a level sufficient to reasonably justify investing in such facilities were also considered in assessing the best available technology economically achievable. It is the highest degree of control technology that has been achieved and has been demonstrated to be capable of being designed for plant scale operation. Although economic factors are considered in this development, the costs for this level of control are intended to be for the top-of-the line of current technology subject to limitations imposed by economic and engineering feasibility. However, this technology may necessitate some industrially sponsored development work prior to its application.

#### EFFLUENT REDUCTION ATTAINABLE USING BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE

Based upon the information contained in Sections III through IX of this report, the following determinations were made on the degree of effluent reduction attainable by the application of the best available control technology economically achievable in the various categories of the inorganic chemical industry.

##### General Water Guidelines

Process water is defined as any water contacting the reactants of a process including contact cooling water. All values of guidelines and limitations presented below are expressed as thirty-day averages in units of kg of parameter per metric ton (lbs/ton) of product produced. The daily maximum limitation is double the monthly average, as discussed in section IX. For those subcategories which utilize impoundments to achieve no discharge of process waste water pollutants, an untreated discharge is allowed in the event of a catastrophic rainfall exceeding the maximum 25 year, 24 hour rainfall event.

No discharge of process waste water pollutants to navigable waters is attainable by the application of the best practicable technology currently available for the following chemical subcategories:

- aluminum chloride
- aluminum sulfate
- calcium carbide
- calcium oxide and calcium hydroxide
- hydrochloric acid
- hydrofluoric acid
- nitric acid
- potassium metal
- potassium dichromate
- potassium sulfate
- sodium bicarbonate
- sulfuric acid

The same effluent reduction is required for these subcategories based on best available technology economically achievable.

##### Calcium Chloride

Best available technology economically achievable includes recycle of the packaging area washdown water and use of noncontact heat exchangers. These process changes are being planned by plant 185.

Therefore, the effluent limitations guidelines for calcium chloride based on the application of the best available technology economically achievable require no discharge of process waste water pollutants to navigable waters.

##### Hydrogen Peroxide

###### a) Organic process

Best available technology for organic process hydrogen peroxide plants is to recycle all process water. The discharged process water presently contains hydrogen peroxide and organic solvent which should not be detrimental to the process. Carbon adsorption techniques may be applied if necessary prior to water reuse. The effectiveness of this treatment for organic removal has been widely demonstrated.

The effluent limitations guidelines for hydrogen peroxide production by the organic process based on the application of the best available technology economically achievable require no discharge of process waste water pollutants to navigable waters.

###### b) Electrolytic process

Best available technology for this process is segregation of the process waste water from the cooling water discharge, treatment of the relatively small amount of process waste water by distillation. The distillate may be reused in the process. This is feasible because the process waste water flow is only 95 l/kg (25 gal/ton) in the one plant using this process.

The effluent limitations guidelines for electrolytic process hydrogen peroxide plants based on the application of the best available technology economically achievable require no discharge of process waste water pollutants to navigable waters.

## Sodium Carbonate

The calcium chloride raw waste load of the Solvay process is such that 10-15 percent of it can supply the total volume of the current U.S. market for calcium chloride, so the potential for waste disposal through this channel may be limited. Large capital costs are involved to bring Solvay process plants to the capability of zero discharge, and the disposal of the by-product calcium chloride is difficult due to its extreme solubility. However, technology does exist to further reduce the concentration of suspended solids in the effluent to 15 mg/l or to reduce the volume of process water required.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after the application of best available technology economically achievable for soda ash produced by the Solvay process:

TSS	0.10 kg/kkg (0.20 lb/ton)
pH	within the range 6.0 to 9.0

## Sodium Chloride

### a) Solar evaporation process

Consistent with the effluent reduction attainable by the application of best practicable technology, unused bitterns may be returned to the brine source provided no additional pollutants are added.

### b) Solution brine-mining process

The major source of the discharged sodium chloride dissolved solids waste generated at plant 030 emanates from carryover in the barometric condensers. The best available technology economically achievable for brine mining evaporative process sodium chloride plants is to replace the barometric condensers with noncontact heat exchangers and recycle the steam condensate to the evaporators. The effluent limitations guidelines for evaporative process sodium chloride plants based on the application of the best available technology economically achievable require no discharge of process waste water pollutants to navigable waters.

## Sodium Metal

Best available technology for sodium metal plants is:

- Recycle of the wastes from cell washdowns to brine purification after removal of suspended solids.
- Recovery of the calcium hypochlorite waste from the tail gas scrubber as a product and recycle of water to the scrubber, or replace the scrubber with a chlorine-burning hydrochloric acid facility.

- Recycle the spent sulfuric acid used for drying the chlorine to a "decomp" sulfuric acid plant or sale as a weak acid solution.

Implementation of these technologies will eliminate the discharge of process waste water pollutants.

The effluent limitations guidelines for sodium metal-chlorine plants based on the application of the best available technology economically achievable require no discharge of process waste water pollutants to navigable waters.

## Sodium Sulfite

Best available technology for sodium sulfite plants is recovery of the sodium sulfate from the waste discharge by evaporation and sale as a by-product or satisfactory land disposal. This should not be too costly since the volume of effluent from plant 168, for example, averages only 1426.5 cu m/day (3700-7000 gal/day), and the dissolved solids in this stream are mostly sodium sulfate.

The effluent limitations guidelines for sodium sulfite plants based on the application of the best available technology economically achievable require no discharge of process waste water pollutants to navigable waters.

## Chlorine and Sodium or Potassium Hydroxide

### a) Diaphragm cell process

Best practicable technology currently available for the manufacture of chlorine and caustic soda or caustic potash by the diaphragm cell process allows the discharge of treated wastes from the tail gas scrubber and of neutralized spent acid from chlorine drying. Best available technology is elimination of the pollutant discharge by:

- Catalytic treatment of the hypochlorite waste from the scrubber to convert to a brine and recycle to brine purification, recovery of the hypochlorite as a bleach product or elimination of the scrubber and utilization of the chlorine gas elsewhere in the plant, such as in a chlorine-burning hydrochloric acid plant;
- Recovery of the spent acid from chlorine drying and sale, utilization elsewhere in the plant or return to spent sulfuric acid plant for regeneration; and
- Recycle of all weak brine/caustic solutions to the process after extraction/elimination of harmful metals and impurities.



The effluent limitations guidelines for diaphragm cell chlor-alkali plants based on the application of the best available technology economically achievable require no discharge of process waste water pollutants to navigable waters.

b) Mercury cell process

The same technologies cited above for diaphragm cell plants apply to mercury cell plants.

The effluent limitations guidelines for mercury cell chlor-alkali plants based on the application of the best available technology economically achievable require no discharge of process waste water pollutants to navigable waters.

Sodium Dichromate and Sodium Sulfate

At plant 184, a total of approximately 113,000 kkg of product and by-product are manufactured annually. The additional treatment cost to this plant for the evaporation of the effluent to effect zero discharge would amount to about \$250,000/yr. This would mean an approximate cost of \$2.20/kkg of sodium dichromate and sodium sulfate.

The effluent limitations guidelines for sodium dichromate and byproduct sodium sulfate plants, based on the application of the best available technology economically achievable require no discharge of process waste water pollutants to navigable waters.

Titanium Dioxide

As indicated in Section VIII of this report, the additional treatment costs projected to bring each of these processes (chloride and sulfate) to zero discharge of process waste water pollutants by demineralization and evaporation of regenerant solutions are as follows:

a. Chloride process - an additional \$730,000 per year for a plant with a 24,300 kkg (27,000 ton) per year capacity or an increase of approximately 5 percent over the costs of best practicable technology.

b. Sulfate process - an additional \$620,000 per year for a plant with a 39,600 kkg (43,000 ton) per year capacity or an increase of approximately 3 percent over the costs of best practicable technology

However, evaporation of the large amounts of water necessary in both processes would consume large amounts of energy and solid waste disposal costs are high. The technology does exist to further reduce the concentration of suspended solids and iron.

Best available technology economically achievable consists of water conservation and more efficient suspended solids removal than required by the 1977 standard. The following limitations constitute the quantity of pollutants which may be discharged after application of the best available technology economically achievable by titanium dioxide plants:

a. Chloride Process:

TSS	1.3 kg/kkg (2.6 lbs/ton)
Iron	0.18 kg/kkg (0.36 lb/ton)
pH	within the range 6.0 to 9.0

b. Sulfate Process:

TSS	5.3 kg/kkg (10.6 lbs/ton)
Iron	0.42 kg/kkg (0.84 lb/ton)
pH	within the range 6.0 to 9.0



## SECTION XI

### NEW SOURCES PERFORMANCE STANDARDS AND PRETREATMENT STANDARDS,

The term "new source" is defined in the Act to mean "any source, the construction of which is commenced after the publication of proposed regulations prescribing a standard of performance". The treatment technology for new sources is evaluated by adding to the considerations underlying the identification of best available technology economically achievable, a determination of what higher levels of pollution control are available through the use of improved production processes and/or treatment techniques. Thus, in addition to considering the best in-plant and end-of-process control technology, new source performance standards reflect how the level of effluent may be reduced by changing the production process itself. Alternative processes, operating methods or other alternatives were considered. However, the end result of the analysis identifies effluent standards which reflect levels of control achievable through the use of improved production processes (as well as control technology), rather than prescribing a particular type of process or technology which must be employed.

The following factors were considered in assessing the best demonstrated control technology currently available for new sources:

- (a) the type of process employed and process changes;
- (b) operating methods;
- (c) batch as opposed to continuous operations;
- (d) use of alternative raw materials and mixes of raw materials;
- (e) use of dry rather than wet processes (including substitution of recoverable solvents for water); and
- (f) recovery of pollutants as by-products.

In addition to the effluent limitations covering discharges directly into waterways, the constituents of the effluent discharge from a plant within the industrial category which would interfere with, pass through, or otherwise be incompatible with a well-designed and operated publicly owned activated sludge or trickling filter waste water treatment plant were identified.

EFFLUENT REDUCTION ATTAINABLE BY THE APPLICATION OF THE BEST AVAILABLE DEMONSTRATED CONTROL TECHNOLOGIES, PROCESSES, OPERATING METHODS OR OTHER ALTERNATIVES.

Based upon the information contained in Sections III through X of this report, the following determinations were made on the degree of effluent reduction attainable with the application of new source standards for the various subcategories of the inorganic chemicals industry.

No discharge of process waste water pollutants to navigable waters is the new source performance standard for the following chemical subcategories:

- aluminum chloride
- aluminum sulfate
- calcium carbide
- hydrochloric acid
- hydrofluoric acid
- calcium oxide and calcium hydroxide
- nitric acid
- potassium metal
- potassium dichromate
- potassium sulfate
- sodium bicarbonate
- sulfuric acid

This is achievable by the application of the best practicable technology currently available.

The new source performance standards for the following chemicals require no discharge of process waste water pollutants to navigable waters:

- calcium chloride
- hydrogen peroxide
- sodium metal
- sodium chloride
  - a) solution brine-mining process

This standard may be achieved by the incorporation of best available technologies economically achievable into new sources. The technologies, as outlined in Section X, have been demonstrated and may be included in the design of new sources.

#### Chlorine

New source performance standards for chlorine are based on the application of best practicable technology currently available, as summarized in Section IX. Metal anodes may be used to eliminate the discharge of lead, as required for new plants.

#### Sodium Carbonate

An alternative process for the manufacture of soda ash with no discharge of process waste water pollutants exists, the mining and processing of trona. Because of this, no discharge of process waste water pollutants to navigable waters is the new source performance standard for this manufacturing process. The calcium chloride raw waste load of the Solvay process is such that 10 to 15 percent of it can supply the total volume of the U.S. market. Large capital costs are involved to bring Solvay process plants to the capability of no discharge, and the disposal of the unmarketable by-product calcium chloride is difficult due to its extreme solubility. No new Solvay process plants have been built in forty years. The supply of trona ore is adequate to satisfy the demand for sodium carbonate.

#### Sodium Chloride

The new source performance standards represent the effluent reduction attainable by the application of the best practicable technology currently available as described in Section IX.

#### Sodium Dichromate and Sodium Sulfate

The new source performance standards for sodium dichromate and by product sodium sulfate plants represent the application of best practicable technology currently available and require good water conservation which is possible in the construction of new facilities.

The new source performance standards for this subcategory are:

TSS	0.15 kg/kg (0.3 lb/ton)
Cr(T)	0.0044 kg/kg (0.0088 lb/ton)
Cr(+6)	0.0005 kg/kg (0.001 lb/ton)
pH	within the range 6.0 to 9.0

#### Titanium Dioxide (Chloride and Sulfate Processes)

Although research is currently being conducted to determine the feasibility of acid recovery and recycle of process water, many problems remain unsolved. As such, it is not considered feasible to require this technology to be incorporated into new facilities. The new source performance standards for titanium dioxide require the same degree of effluent reduction attainable by the application of best available technology economically achievable, as presented in Section X. This technology is demonstrated and may be applied to new sources.

#### PRETREATMENT STANDARDS FOR NEW SOURCES

Plants whose waste water discharges are characterized by the presence of materials that interfere with operation of biological systems are not suited to use of conventional secondary waste

treatment. Extreme segregation (that is, limiting the sewerage discharge to sanitary and other organic wastes) or pretreatment is required by such manufacturing plants.

The pretreatment standards for new sources in the inorganic chemicals manufacturing category are the standards set forth in 40 CFR 128. In addition to these standards, however, the pretreatment standard for incompatible pollutants is the new source performance standard. If a publicly owned treatment works is committed to remove a specified percentage of any incompatible pollutant, the pretreatment standard is correspondingly reduced in stringency for that pollutant.

## SECTION XII

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## SECTION XIV

### GLOSSARY

#### Acidity

The total titratable hydrogen ion content of the solution is defined as the acidity. Acidity is expressed in mg/l of free hydrogen ion.

#### Adsorption

Condensation of the atoms, ions or molecules of a gas, liquid or dissolved substance on the surface of a solid called the adsorbent. The best known examples are gas/solid and liquid/solid systems.

#### Air Pollution

The presence in the air of one or more air contaminants in quantities injurious to human, plant, animal life, or property, or which unreasonably interferes with the comfortable enjoyment thereof.

#### Alkalinity

Total titratable hydroxyl ion concentration of a solution. In water analysis, alkalinity is expressed in mg/l (parts per million) of calcium carbonate.

#### Ash

The solid residue left after incineration in the presence of oxygen.

#### Bag Filter

A dry collection device for recovery of particulate matter from gas streams.

#### Barometric Condenser

Device, operating at barometric pressure, used to change vapor into liquid by cooling.

#### Blowdown

The minimum discharge of recirculating water for the purpose of discharging materials contained in the water, the further build-up of which would cause concentration in amounts exceeding limits established by best engineering practice.

### Brine

An aqueous salt solution.

### Calcination

The roasting or burning of any substance to bring about physical or chemical changes; e.g., the conversion of limestone to quicklime.

### Carbonation

Treatment with carbon dioxide gas.

### Catalytic Converter

A unit containing a packed or fluidized bed of catalyst.

### Caustic

Capable of destroying or eating away by chemical action. Applied to strong bases and characterized by the presence of hydroxyl ions in solution.

### Centrifuge

A device having a rotating container in which centrifugal force separates substances of differing densities.

### Chemical Oxygen Demand, COD

Its determination provides a measure of the quantity of oxygen required to oxidize the organic matter (or other oxidizable matter) in a waste sample, under specific conditions of oxidizing agents, temperature and time. The general method is applied to waste samples having an organic carbon concentration greater than 15 mg/l.

### Coke

The carbonaceous residue of the destructive distillation (carbonization) of coal or petroleum.

### Conditioning

A physical and/or chemical treatment given to water used in the plant or discharged.

### Conductivity, Electrical

The ability of a material to conduct a quantity of electricity transferred across a unit area, per unit potential gradient per

unit time. In practical terms, it is used for approximating the salinity or total dissolved solids content of water.

### Cooling Water

Water which is used to absorb waste heat generated in the process. Cooling water can be either contact or noncontact.

### Copperas

Ferrous sulfate.

### Cyclone Separator

A mechanical device which removes suspended solids from gas streams.

### Demineralization

The removal from water of mineral contaminants usually present in ionized form. The methods used include ion-exchange techniques, flash distillation or electrolysis.

### Electrostatic Precipitator

A gas cleaning device using the principle of placing an electrical charge on a solid particle which is then attracted to an oppositely-charged collector plate.

### Filtrate

Liquid after passing through a filter.

### Filtration

Removal of solid particles from liquid or particles from air or gas stream through a permeable membrane.

### Flocculation

The combination of aggregation of suspended solid particles in such a way that they form small clumps. The term is used as a synonym for coagulation.

### Fluidized Bed Reactor

A reactor in which finely divided solids are caused to behave like fluids due to their suspension in a moving gas or liquid stream.

### Gas Washer (or Wet Scrubber)

Apparatus used to remove entrained solids and other substances from a gas stream.

#### Hardness (Total)

The characteristic of water generally accepted to represent the total concentration of calcium and magnesium ions, usually expressed as mg/l of calcium carbonate.

#### Heavy Metal

One of the metal elements not belonging to the alkali or alkaline earth group. In this study, the classification includes titanium, vanadium, iron, nickel, copper, mercury, lead, cadmium, and chromium.

#### Ion Exchange

A reversible chemical reaction between a solid and a fluid by means of which ions may be interchanged from one substance to another. The customary procedure is to pass the fluid through a bed of the solid, which is granular and porous and has a limited capacity for exchange. The process is essentially a batch type in which the ion exchanger, upon nearing depletion, is regenerated by inexpensive salts or acid.

#### Kiln (Rotary)

A large cylindrical mechanized type of furnace used for calcination.

#### Membrane

A thin sheet of synthetic polymer, through the apertures of which small molecules can pass, while larger ones are retained.

#### Mother liquor

The solution from which crystals are formed.

#### Multi-Effect Evaporator

In chemical processing installations, requiring a series of evaporations and condensations, the individual units are set up in series and the latent heat of vaporization from one unit is used to supply energy for the next. Such units are called "effects" in engineering parlance as, e.g., a triple effect evaporator.

#### Oleum or Fuming Sulfuric Acid

A solution of sulfur trioxide in sulfuric acid.

#### pH

Is a measure of the relative acidity or alkalinity of water. A pH value of 7.0 indicates a neutral condition; less than 7 indicates a predominance of acids, and greater than 7, a predominance of alkalis. There is a 10-fold increase (or decrease) from one pH unit level to the next, e.g., 10-fold increase in alkalinity from pH 8 to pH 9.

#### Plant Effluent or Discharge after Treatment

The waste water discharged from the industrial plant. In this definition, any waste treatment device (pond, trickling filter, etc.) is considered part of the industrial plant.

#### Pretreatment

The necessary processing given materials before they can be properly utilized in a process or treatment facility.

#### Process Effluent or Discharge

The volume of waste water emerging from a particular use in the plant.

#### Process Water

Water which is used in the internal plant streams from which products are ultimately recovered, or water which contacts either the raw materials or product at any time.

#### Reverse Osmosis

A method involving application of pressure to the surface of a saline solution forcing water from the solution to pass from the solution through a membrane which is too dense to permit passage of salt ions. Hollow nylon fibers or cellulose acetate sheets are used as membranes since their large surface areas offer more efficient separation.

#### Sedimentation

The falling or settling of solid particles in a liquid, as a sediment.

#### Settling Pond

A large shallow body of water into which industrial waste waters are discharged. Suspended solids settle from the waste waters due to the large retention time of water in the pond.

#### Sintering



The agglomeration of powders at temperatures below their melting points. Sintering increases strength and density of the powders.

#### Slaking

The process of reacting lime with water to yield a hydrated product.

#### Sludge

The settled mud from a thickener clarifier. Generally, almost any flocculated, settled mass.

#### Slurry

A watery suspension of solid materials.

#### Sniff Gas

The exhaust or tail gas effluent from the chlorine liquefaction and compression portion of a chlor-alkali facility.

#### Solute

A dissolved substance.

#### Solvent

A liquid used to dissolve materials.

#### Thickener

A device or system wherein the solid contents of slurries or suspensions are increased by evaporation of part of the liquid phase, or by gravity settling and mechanical separation of the phases.

#### Total Dissolved Solids (TDS)

The total amount of dissolved solid materials present in an aqueous solution.

#### Total Organic Carbon, TOC

A measurement of the total organic carbon content of surface waters, domestic and industrial wastes, and saline waters.

#### Total Suspended Solids (TSS)

Solid particulate matter found in waste water streams, which, in most cases, can be minimized by filtration or settling ponds.

#### Turbidity

A measure of the opacity or transparency of a sediment-containing waste stream. Usually expressed in Jackson units or Formazin units which are essentially equivalent in the range below 100 units.

#### Wet Scrubbing

A gas cleaning system using water or some suitable liquid to entrap particulate matter, fumes, and absorbable gases.

#### Waste Discharged

The amount (usually expressed as weight) of some residual substance which is suspended or dissolved in the plant effluent.

#### Waste Generated (Raw Waste)

The amount (usually expressed as weight) of some residual substance generated by a plant process or the plant as a whole. This quantity is measured before treatment.

#### Water Recirculation or Recycling

The volume of water already used for some purpose in the plant which is returned with or without treatment to be used again in the same or another process.

#### Water Use

The total volume of water applied to various uses in the plant. It is the sum of water recirculation and water withdrawal.

#### Water Withdrawal or Intake

The volume of fresh water removed from a surface or underground water source by plant facilities or obtained from some source external to the plant. The effluent limitations guidelines for sodium dichromate and byproduct sodium sulfate plants, based on the application of the best available technology economically achievable, require no discharge of process waste water pollutants to navigable waters. 9992;G